

2.0 Source Emission Estimates Using CHEMDAT8

This section describes the CHEMDAT8 emission model used to develop emission estimates for each WMU. Section 2.1 describes why CHEMDAT8 was chosen and provides an overview of CHEMDAT8; Section 2.2 provides scientific background on emissions modeling for aqueous- versus organic-phase wastes; Section 2.3 describes the input parameters; and Section 2.4 describes the important modeling assumptions and equations used to calculate mass emission rates.

2.1 Model Selection and Overview of CHEMDAT8

EPA's CHEMDAT8 model was selected as the model to estimate volatile emission rates from the WMUs in IWAIR. CHEMDAT8 meets the goals that were established during the model selection process. EPA sought to select a model that

- Provides emission estimates that are as accurate as possible without underestimating the constituent emissions
- Provides a relatively consistent modeling approach (in terms of model complexity and conservatism) for each of the different emission sources under consideration
- Has undergone extensive peer review and is widely accepted by both EPA and industry
- Is publicly available for use in more site-specific evaluations.

The CHEMDAT8 model was originally developed in projects funded by EPA's Office of Research and Development (ORD) and Office of Air Quality Planning and Standards (OAQPS) to support National Emission Standards for Hazardous Air Pollutants (NESHAPs) from sources such as tanks, surface impoundments, landfills, waste piles, and land application units for a variety of industry categories, including chemical manufacturers, pulp and paper manufacturing, and petroleum refining. CHEMDAT8 includes analytical models for estimating volatile compound emissions from treatment, storage, and disposal facility processes under user-specified input parameters and has been used to support the emissions standards for hazardous waste treatment, storage, and disposal facilities (U.S. EPA, 1991) regulated under Subpart CC rules of the Resource Conservation and Recovery Act (RCRA), as amended in 1984. The CHEMDAT8 model is publicly available and has undergone extensive review by both EPA and industry representatives.

CHEMDAT8 models volatile air emissions and considers most of the significant competing removal pathways that might limit those emissions (see text box). These competing removal pathways lower the potential for emission to the air as gases in various ways: adsorption limits the mass of chemical free to volatilize by binding chemical on the waste particles; biodegradation and hydrolysis reduce the mass of the chemical in the unit (although these mechanisms do generate new chemicals in the form of breakdown products); and leaching and runoff remove chemical mass from the unit by non-air pathways (i.e., to groundwater or surface water).

For surface impoundments, CHEMDAT8 considers adsorption, biodegradation, and hydrolysis. For land application units, landfills, and waste piles, CHEMDAT8 considers biodegradation; CHEMDAT8 does not explicitly consider adsorption for these unit types, but volatilization from these unit types is limited by the relative air porosity of the soil or waste matrix. CHEMDAT8 does not consider hydrolysis in the land application unit, landfill, and waste pile, even for soil moisture or percolating rainwater. CHEMDAT8 does not consider leaching or runoff for any of the unit types, nor does it model chemical breakdown products from biodegradation or hydrolysis. As such, CHEMDAT8 is considered to provide reasonable to slightly high (environmentally conservative) estimates of air emissions from the various emission sources modeled in IWAIR.

EPA's CHEMDAT8 model is a modular component of IWAIR. The original CHEMDAT8 Lotus 1-2-3 spreadsheet was converted to Visual Basic code for use in IWAIR. In addition, the chemical-specific data in the original code were evaluated for accuracy. Some of these values have been changed to reflect newer or better information. A list of the physical-chemical property values included in IWAIR is provided in Appendix B of this document. Extensive testing was performed to ensure that the coded version produces results identical to the spreadsheet version.

This document provides information about CHEMDAT8 that is pertinent to the IWAIR program, including the CHEMDAT8 equations used in IWAIR. However, it does not attempt to reproduce the CHEMDAT8 documentation, so the equations are presented, but their derivation is not covered in any detail. For complete documentation on the CHEMDAT8 model, refer to documents available on EPA's Web page. The CHEMDAT8 spreadsheet model and model documentation may be downloaded at no charge from EPA's Web page (<http://www.epa.gov/ttn/chief/software.html>).

Competing Removal Pathways

Adsorption is the tendency of a chemical or liquid medium to attach or bind to the surface of particles in the waste.

Biodegradation is the tendency of a chemical to be broken down or decomposed into less-complex chemicals by organisms in the waste or soil.

Hydrolysis is the tendency of a chemical to be broken down or decomposed into less-complex chemicals by reaction with water in the waste or soil.

Leaching is the tendency of a chemical to dissolve in water in the waste or soil and follow the flow of water (e.g., due to rainfall) down through the soil to groundwater.

Runoff is the tendency of a chemical to dissolve in water in the waste or soil and follow the flow of water (e.g., due to rainfall) downhill to surface water.

2.2 Scientific Background

A WMU contains solids, liquids (such as water), and air. Individual chemical molecules are constantly moving from one of these media to another: they may be adsorbed to solids, dissolved in liquids, or assume vapor form in air. At equilibrium, the movement into and out of each medium is equal, so that the concentration of the chemical in each medium is constant. The emissions model used in IWAIR, CHEMDAT8, assumes that equilibrium has been reached.

Partitioning refers to how a chemical tends to distribute itself among these different media. Different chemicals have differing affinities for particular phases—some chemicals tend to partition preferentially to air, while others tend to partition preferentially to water. The different tendencies of different chemicals are described by partition coefficients or equilibrium constants.

Of particular interest in modeling volatile emissions of a chemical from a liquid waste matrix is the chemical's tendency to change from a liquid form to a vapor form. As a general rule, a chemical's vapor pressure describes this tendency. The pure-component vapor pressure is a measure of this tendency for the pure chemical. A chemical in solution in another liquid (such as a waste containing multiple chemicals) will exhibit a partial vapor pressure, which is the chemical's share of the overall vapor pressure of the mixture; this partial vapor pressure is lower than the pure-component vapor pressure and is generally equal to the pure-component vapor pressure times the constituent's mole fraction (a measure of concentration reflecting the number of molecules of the chemical per unit of volume) in the solution. This general rule is known as Raoult's law.

Most chemicals do not obey Raoult's law in dilute (i.e., low concentration) aqueous solutions, but exhibit a greater tendency to partition to the vapor phase from dilute solutions than would be predicted by Raoult's law. These chemicals exhibit a higher partial vapor pressure than the direct mole fraction described above would predict.¹ This altered tendency to partition to the vapor phase in dilute solutions is referred to as Henry's law. To calculate the emissions of a constituent from a dilute solution, a partition coefficient called Henry's law constant is used. Henry's law constant relates the partial vapor pressure to the concentration in the solution.

To account for these differences in the tendency of chemicals to partition to vapor phase from different types of liquid waste matrices, CHEMDAT8 models emissions in two regimes: a dilute aqueous phase, modeled using Henry's law constant as the partition coefficient, and an organic phase, modeled using the partial vapor pressure predicted by Raoult's law as the partition coefficient. In fact, there is not a clear point at which wastes shift from dilute aqueous phase to organic phase; this is a model simplification. However, several rules of thumb are used to determine when the Raoult's law model would be more appropriate. The clearest rule is that any chemical present in excess of its solubility limit in a wastewater or its saturation concentration in soil has exceeded the bounds of "dilute aqueous" and is more appropriately modeled using

¹ There are some exceptions to this behavior in dilute solutions. A notable exception is formaldehyde, which has lower activity in dilute aqueous solution, which means that formaldehyde will have greater emissions in a high-concentration organic-phase waste.

Raoult's law. Chemicals exceeding solubility or saturation limits will typically come out of solution and behave more like pure, organic-phase component. However, solubility and saturation limits can vary depending on site-specific parameters, such as temperature and pH of the waste. In addition, waste matrix effects² can cause chemicals to remain in solution at concentrations above their typical solubility or saturation limit. This scenario (an aqueous-phase waste with concentrations above typical solubility or saturation limits) is also best modeled using Raoult's law.

Another rule of thumb is that a waste with a total organics concentration in excess of about 10 percent (or 100,000 ppm) is likely to behave more like an organic-phase waste than a dilute aqueous-phase waste and be more appropriately modeled using Raoult's law.

Aqueous-phase waste: a waste that is predominantly water, with low concentrations of organics. All chemicals remain in solution in the waste and are usually present at concentrations below typical solubility or saturation limits. However, it is possible for the specific components of the waste to raise the effective solubility or saturation level for a chemical, allowing it to remain in solution at concentrations above the typical solubility or saturation limit.

Organic-phase waste: a waste that is predominantly organic chemicals, with a high concentration of organics. Concentrations of some chemicals may exceed solubility or saturation limits, causing those chemicals to come out of solution and form areas of free product in the WMU. In surface impoundments, this can result in a thin organic film over the entire surface.

For land application units, landfills, and waste piles, where the waste is either a solid or mixed with a solid (such as soil), the CHEMDAT8 emissions model considers two-phase partitioning of the waste into the liquid (either aqueous or organic) phase and the air phase, using the partition coefficients described above, to estimate the equilibrium vapor composition in the pore (or air) space within the WMU. Emissions are subsequently estimated from the WMU by calculating the rate of diffusion of the vapor-phase constituent through the porous waste/soil medium.

For surface impoundments, where the waste is a liquid, the model uses a different approach that considers the resistance to mass transfer (i.e., movement of chemical mass from one phase to the other) in the liquid and gas phases at the surface of the impoundment. Emissions are calculated using an overall mass transfer coefficient, which is based on the partition coefficient (as described above), the liquid-phase mass transfer factor (which accounts for resistance to transfer in the liquid phase), and the gas-phase mass transfer factor (which accounts for resistance to transfer in the gas phase). This is referred to as the two-film model. For organic-phase wastes, the mass transfer is dominated by the gas-phase resistance and the partition coefficient; the liquid-phase mass transfer resistance is negligible and is, therefore, omitted from the calculation. This is referred to as the one-film model, or the oily film model.

² "Waste matrix effects" refers to the effect that the composition of the waste has on a constituent's solubility in the waste or the tendency for the chemical to evaporate from the waste. For example, hexane has a solubility in distilled water of approximately 12 mg/L; however, its solubility in methanol is much higher (more than 100,000 mg/L) (Perry and Green, 1984). Therefore, it is likely that hexane will remain dissolved in a solution of 10 percent methanol in water at higher concentrations than the aqueous solubility limit of 12 mg/L suggests.

In the two-film model for surface impoundments, the gas-phase and liquid mass transfer coefficients are strongly affected by the turbulence of the surface impoundment's surface. Turbulence may be caused by mechanical aeration or, to a lesser extent, diffused air aeration. Therefore, whether the impoundment is aerated or not and how it is aerated are important inputs.

2.3 Emission Model Input Parameters

To model emissions using CHEMDAT8, users enter unit-specific data. Most of the inputs are used by CHEMDAT8 directly, but some are used to calculate other inputs for CHEMDAT8. The IWAIR program provides default input data for some parameters. For example, the annual average temperature and wind speed for a WMU site are automatically used as a default for a site once the site is assigned to one of the 60 meteorological stations in the IWAIR program. Users may choose to override the default data and enter their own estimates for these parameters. Thus, emissions can be modeled using CHEMDAT8 with a very limited amount of site-specific information by using the default data provided.

This section discusses the various parameters that have a significant impact on the estimated emission rates. Inputs that influence these rates include

- Input parameters specific to the physical and chemical properties of the constituent being modeled
- The characteristics of the waste material being managed
- Input parameters specific to the process and operating conditions of the WMU being modeled
- Meteorological parameters.

IWAIR checks inputs only against the limits of the model or absolute physical limits (e.g., area must be greater than zero). It does not verify that user-provided inputs are within some “typical” or “acceptable” range. However, Appendix B of the *IWAIR User's Guide* provides guidance for developing values for all input parameters.

A general discussion of the physical and chemical properties of the constituents is provided in the Section 2.3.1. Critical input parameters for the remaining sets of inputs are discussed for land application units, landfills, and waste piles in Section 2.3.2 and for surface impoundments in Section 2.3.3. The input parameters used in IWAIR differ in some respects from those needed by CHEMDAT8. When the CHEMDAT8 inputs are not readily available but can be calculated from more readily available data, IWAIR uses the more readily available input parameters. The equations used to convert these to the CHEMDAT8 inputs are documented in Section 2.4. For detailed guidance on developing input values for all parameters needed to run IWAIR, see Appendix B, “Parameter Guidance,” of the *IWAIR User's Guide*.

2.3.1 Chemical-Specific Input Parameters

Chemical-specific input parameters are those parameters that relate to the physical or chemical properties of each individual chemical. The values of these parameters are different for each of the 95 chemicals included in IWAIR. Table 2-1 lists the chemical-specific input parameters needed to run IWAIR, along with minimum and maximum values, if any (a blank in the maximum column indicates that no maximum value is enforced). IWAIR comes with chemical data for 95 chemicals in its chemical properties database. Using the ADD/MODIFY CHEMICALS feature, the user can create additional entries in the chemical properties database to reflect different property values for organic chemicals included in IWAIR or to add new organic chemicals not included in IWAIR. To maintain the integrity of the original chemical data included with IWAIR, those entries cannot be edited directly; however, they may be used as the basis for new entries. Mercury is included in the IWAIR database in both divalent and elemental forms, but because of code modifications needed for mercury (to reflect differences in its behavior, since it is not an organic chemical), the user may not create additional or modified entries for mercury.

Organic Chemicals

The IWAIR model covers only organic chemicals, with the exception of mercury. Organic chemicals are those pertaining to or derived from living organisms. All organic chemicals contain carbon and most also contain hydrogen, although there are some substituted carbon compounds that do not contain hydrogen but are generally considered to be organics (e.g., carbon tetrachloride). However, elemental carbon and certain other carbon-containing compounds (e.g., carbon dioxide) are considered inorganic compounds.

Key chemical-specific input parameters that have a significant impact on modeled emissions include air-liquid equilibrium partition coefficients (vapor pressure or Henry's law constant), liquid-solid equilibrium partition coefficients (log octanol-water partition coefficient for organics), biodegradation rate constants, and liquid and air diffusivities.

The primary data sources for the physical and chemical properties for the constituents included in IWAIR include

- EPA's Superfund Chemical Data Matrix (SCDM) (U.S. EPA, 1997d),
- The Merck Index (Budavari, 1996),
- The National Library of Medicine's Hazardous Substances Databank (HSDB), available on TOXNET (U.S. NLM, 2001),
- Syracuse Research Corporation's CHEMFATE database (SRC, 1999)
- CambridgeSoft.com's ChemFinder database (CambridgeSoft, 2001),
- EPA's *Mercury Report to Congress* (U.S. EPA, 1997c), and
- EPA's *Dioxin Reassessment* (U.S. EPA, 2000).

Table 2-1. Chemical-Specific Inputs

Parameter	Minimum Value	Maximum Value ^a	Comments
Chemical name			Cannot be left blank; maximum length is 60 characters
CAS number			Cannot be left blank; must be numeric; maximum length is 9 numbers
Molecular weight (g/mol)	1		
Density (g/cm ³)	>0		
Vapor pressure (mm Hg)	>0		
Henry's law constant (atm · m ³ /mol)	>0		
Solubility (mg/L)	>0	1,000,000	
Diffusivity in water (cm ² /s)	>0		
Diffusivity in air (cm ² /s)	0		
Log K _{ow}	-10	10	
K ₁ (L/g-h)	0		User-entered values of zero are changed to 1E-6 to prevent division by zero in IWAIR.
K _{max} (mg VO/g-h)	0		User-entered values of zero are changed to 1E-4 to prevent division by zero in IWAIR.
Soil biodegradation rate (s ⁻¹)	0		User-entered values of zero are changed to 1E-20 to prevent division by zero in IWAIR.
Hydrolysis constant (s ⁻¹)	0		
Antoine's constant A	0		
Antoine's constant B	0		
Antoine's constant C	None		
Soil saturation concentration (mg/kg)	>0		Calculated by IWAIR

^a A blank cell indicates there is no maximum value.

These sources were used for molecular weight, density, vapor pressure, Henry's law constant, solubility, and log octanol-water partition coefficient. Liquid and air diffusivities were calculated from other properties. Antoine's coefficients (for adjusting vapor pressure to temperature) were taken from Reid et al. (1977). Soil biodegradation rate constants were taken from Howard et al. (1991). Hydrolysis rate constants were taken from Kollig (1993). Biodegradation rates for surface impoundments (K_i and K_{max}) were taken from CHEMDAT8's chemical properties database (U.S. EPA, 1994a). The surface impoundment biodegradation rate constants in the downloaded CHEMDAT8 database file were compared with the values reported in the summary report that provided the basis for the CHEMDAT8 surface impoundment biodegradation rate values (Coburn et al., 1988). Surface impoundment biodegradation rate constants for compounds with no data were assigned biodegradation rates equal to the most similar compound in the biodegradation rate database. The specific chemical property inputs used for the emission modeling are provided in Appendix B with their chemical- and property-specific references. The following subsections briefly describe each chemical property.

Molecular Weight (g/mol). Molecular weight is used to estimate emissions. This value must be greater than or equal to 1 g/mol (the molecular weight of a single hydrogen ion).

Density (g/m³). IWAIR uses density to determine if chemicals present in organic phase in surface impoundments are likely to float (if they are less dense than water) or sink (if they are more dense than water). Unless the value is very near 1 g/m³ (the density of water), the model is not sensitive to variations in the value.

Vapor Pressure (mmHg). Vapor pressure and the mole fraction concentration in the liquid phase are used to calculate the constituent's partial vapor pressure. The partial vapor pressure is subsequently used as the partition coefficient for organic-phase wastes and aqueous-phase wastes with chemicals present above solubility or saturation limits. Different vapor pressures may be reported for the same chemical at different temperatures. The vapor pressures in IWAIR were chosen for temperatures as close to 25°C as possible. IWAIR corrects these to the ambient temperature (see Sections 2.4.1 and 2.4.4.1 for specific equations, and Sections 2.3.2 and 2.3.3 for a more general discussion of temperature corrections).

Henry's Law Constant (atm-m³/mol). Henry's law constant reflects the tendency of chemicals to volatilize from dilute aqueous solutions; it is used as the partition coefficient for aqueous-phase wastes with chemicals present below solubility or saturation limits. Values can be obtained from the literature, or they can be calculated from the chemical's vapor pressure, molecular weight, and solubility using the following equation (Lyman et al., 1990):

$$H = \frac{\left(\frac{VP}{760}\right)}{\left(\left(\frac{S}{MW}\right) \times \left(\frac{1000}{1000}\right)\right)} \quad (2-1)$$

where

H	=	Henry's law constant (atm-m ³ /mol)
VP	=	vapor pressure (mmHg)
S	=	solubility (mg/L)
MW	=	molecular weight (g/mol)
760	=	unit conversion (mmHg/atm)
1000	=	unit conversion (L/m ³)
1000	=	unit conversion (mg/g).

IWAIR corrects Henry's law constant to the ambient temperature (see Sections 2.4.1 and 2.4.4.1 for specific equations, and Sections 2.3.2 and 2.3.3 for a more general discussion of temperature corrections).

Solubility (mg/L). This is the solubility of the individual chemical in water. Solubility is used for surface impoundments to identify wastes that may be supersaturated so that emissions equations may be based on the most appropriate partition coefficient (Henry's law for aqueous-phase wastes below saturation or solubility limits, and partial vapor pressure for wastes above saturation or solubility limits and organic-phase wastes).

Soil Biodegradation Rate (s⁻¹). The soil biodegradation rate is a first-order rate constant used to estimate soil biodegradation losses in land application units, landfills, and waste piles. The tendency to biodegrade in soil is often reported as half-life. Half-life is not comparable to biodegradation rate; however, the soil biodegradation rate can be calculated from the half-life as follows:

$$k_s = \frac{\ln(2)}{t_{1/2}} \quad (2-2)$$

where

k_s	=	soil biodegradation rate (s ⁻¹)
$\ln(2)$	=	natural log of 2
$t_{1/2}$	=	half-life (s).

For IWAIR, the longest half-life (i.e., slowest degradation) was chosen when a range of values was reported. Observed biodegradation rates are dependent on the population of specific degrading species, microorganism acclimation, and primary versus secondary substrate utilization. In addition, there is the potential for co-metabolism and inhibition. Consequently, observed biodegradation rates for similar treatment units within the same (or similar) industry are highly variable. Order-of-magnitude variations in observed degradation rates are not unusual. This makes the development of generally applicable biodegradation rate constants a difficult task and ensures a significant level of uncertainty. As a result, users are encouraged to create new chemical entries in the IWAIR database and enter site-specific biodegradation rates if these are available.

Antoine's Constants: A, B, or C. Antoine's constants are used to adjust vapor pressure and Henry's law constant to ambient temperature.

Diffusivity in Water (cm^2/s). Diffusivity in water is used to estimate emissions. Diffusivity in water can be calculated from the chemical's molecular weight and density, using the following correlation equation based on Water9 (U.S. EPA, 2001b):

$$D_w = 0.0001518 \times \left(\frac{T + 273.16}{298.16} \right) \times \left(\frac{\text{MW}}{\rho} \right)^{-0.6} \quad (2-3)$$

where

D_w	=	diffusivity in water (cm^2/s)
T	=	temperature ($^{\circ}\text{C}$)
273.16	=	unit conversion ($^{\circ}\text{C}$ to $^{\circ}\text{K}$)
MW	=	molecular weight (g/mol)
ρ	=	density of chemical (g/cm^3).

If density is not available, diffusivity in water can be calculated using the following correlation equation based on U.S. EPA (1987b):

$$D_w = 0.00022 \times (\text{MW})^{-\frac{2}{3}} \quad (2-4)$$

Diffusivity in Air (cm^2/s). Diffusivity in air is used to estimate emissions. Diffusivity in air can be calculated from the chemical's molecular weight and density, using the following correlation equation based on Water9 (U.S. EPA, 2001b):

$$D_a = \frac{0.00229 \times (T + 273.16)^{1.5} \times \sqrt{0.034 + \left(\frac{1}{\text{MW}} \right)} \times \text{MW}_{\text{cor}}}{\left(\left(\frac{\text{MW}}{2.5 \times \rho} \right)^{0.333} + 1.8 \right)^2} \quad (2-5)$$

where

D_a	=	diffusivity in air (cm^2/s)
T	=	temperature ($^{\circ}\text{C}$)
273.16	=	unit conversion ($^{\circ}\text{C}$ to $^{\circ}\text{K}$)
MW	=	molecular weight (g/mol)
ρ	=	density (g/cm^3)
MW_{cor}	=	molecular weight correlation:

$$MW_{\text{cor}} = (1 - 0.000015 \times MW^2) \quad (2-6)$$

If MW_{cor} is less than 0.4, then MW_{cor} is set to 0.4.

If density is not available, diffusivity in air can be calculated using the following correlation equation based on U.S. EPA (1987b):

$$D_a = 1.9 \times \left(MW^{-\frac{2}{3}} \right) \quad (2-7)$$

For dioxins, diffusivity in air is calculated from the molecular weight using the following equation based on EPA's *Dioxin Reassessment* (U.S. EPA, 2000):

$$D_a = \left(\frac{154}{MW} \right)^{0.5} \times 0.068 \quad (2-8)$$

Octanol-Water Partition Coefficient ($\log K_{ow}$). K_{ow} is used to estimate emissions and to calculate the soil saturation concentration limit for land application units, landfills, and waste piles. Because K_{ow} can cover an extremely wide range of values, it is typically reported as the log of K_{ow} . Mercury does not have a K_{ow} because it is not an organic chemical. The soil-water partition coefficient (K_d) for mercury is used instead.

Hydrolysis Constant (s^{-1}). This value, which is used to estimate losses by hydrolysis, is the hydrolysis rate constant at neutral pH. Very few data were available on hydrolysis rates for IWAIR chemicals; therefore, only a few chemicals have them in the IWAIR database.

K_l (L/g-h) and K_{max} (mg volatile organics/g-h). K_l and K_{max} are used to estimate biodegradation losses in surface impoundments. IWAIR uses the CHEMDAT8 model equations for biodegradation in wastewater treatment units. These biodegradation rate equations are based on the Monod model for biodegradation (analogous to Michaelis-Menten enzyme kinetics). This biodegradation rate model is linear (first order) with constituent concentrations at low concentrations and becomes independent (zero order) at higher concentrations. Unfortunately, because of the difficulty in determining the two biodegradation rate constants (K_l and K_{max}) needed for the Monod model, many detailed wastewater treatment source models resort to simple first-order biodegradation rate kinetics. Although inhibitory kinetics are not included in the model, by using the Monod biodegradation rate model, IWAIR provides a much better simulation of the reduced relative importance of biodegradation at high constituent concentrations than it would if it employed strictly first-order biodegradation kinetics. To include inhibitory kinetics requires a third rate constant, which is available for far fewer compounds than those used as the basis for the Monod constants.

The data sources for the biodegradation rate constants developed for the CHEMDAT8 model and used in IWAIR are fully documented in Coburn et al. (1988); a representative (although incomplete) list of the data sources includes EPA sampling at 10 different activated sludge systems and three surface impoundment units at varied industries; other full-scale sampling studies of activated sludge systems (Berglund and Whipple, 1987; Hannah et al., 1986) and surface impoundments (Demirjian et al., 1983); pilot-scale treatment studies (Petrasek, 1981; Petrasek et al., 1983; and Lesiecki et al., 1987); biodegradability flask studies (Pitter, 1976); and laboratory studies (Kincannon et al., 1982; Beltrame et al., 1980, 1982; and Beltrame, Beltrame, and Carniti, 1982). Although the biodegradation rate constants for the CHEMDAT8 model were developed in 1988, few additional data have been presented since to significantly alter these rate constants.

Biodegradation rate constants were not available for all of the IWAIR compounds. Biodegradation rate constants for compounds that did not have sufficient data were assigned the biodegradation rate constant of the most similar compound (in terms of chemical structure and biologically important functional groups) for which biodegradation rate constants could be estimated. There is some additional uncertainty for these biodegradation rate constants, but similarly structured chemicals typically have similar biodegradation rates, and the added uncertainty in the biodegradation rate constant assignments is likely not much greater than the uncertainty in the biodegradation rate constants themselves.

Soil Saturation Concentration (mg/kg). The soil saturation limit (C_{sat}) reflects the maximum concentration of a chemical that can be present in a soil matrix. C_{sat} is dependent on site-specific factors, as well as chemical properties; therefore, IWAIR calculates it from user inputs as follows:

$$C_{sat} = \frac{S}{\rho_b} (K_d \times \rho_b + \epsilon_w + H' \times \epsilon_a) \quad (2-9)$$

where

- C_{sat} = soil saturation limit (mg/kg)
- S = solubility (mg/L)
- ρ_b = bulk density of soil/waste matrix (kg/L)
- K_d = soil-water partition coefficient (L/kg), calculated as shown below for organic chemicals; this is an input for mercury
- ϵ_w = water-filled porosity (unitless)
- H' = dimensionless Henry's law constant (unitless = H/RT)
- ϵ_a = air-filled porosity (unitless)

and

$$K_d = K_{oc} \times f_{oc} \quad (2-10)$$

where

K_{oc} = organic carbon partition coefficient (L/kg), calculated as shown below
 f_{oc} = fraction organic carbon in waste (unitless).

Fraction organic carbon is set to a fixed value of 0.014. This value was derived from the median of a set of values for many (but not all) of the locations included in the IWAIR dispersion factor database. K_{oc} is calculated as follows (Hasset et al., 1980):

$$K_{oc} = 10^{(\log K_{ow} - 0.32)} \quad (2-11)$$

where

K_{ow} = octanol-water partition coefficient (L/kg).

2.3.2 Input Parameters for Land Application Units, Landfills, and Waste Piles

The input parameters for land-based units are presented in Tables 2-2 through 2-4.

Unit Design and Operating Parameters. The annual waste quantity, the frequency of constituent addition, and the dimensions of the unit influence a number of model input parameters. Because these are so critical and because the values of these parameters for a specific unit to be modeled should be readily available to the user, no default values are provided for these parameters. Operating life is also included here, although it does not affect emissions for waste piles. This value is used to cap the default exposure durations used by IWAIR for landfills and waste piles (30 years for residents and 7.2 years for workers) if the unit is not going to be operating that much longer, as closure of these unit types is assumed to end exposure. Postclosure exposure is assumed to occur for land application units; therefore, exposure duration is not capped at operating life.

Also in this category is the biodegradation toggle. This option lets the user choose whether to model biodegradation losses in the unit. This is set on by default for land application units, which are designed to biodegrade wastes, and off for landfills and waste piles, which often are not.

Waste Characterization. In order to generate an accurate estimate of a constituent's volatile emissions, a user of IWAIR must define the physical and chemical characteristics of the waste that will be managed in the WMU. In particular, the user must identify whether or not the waste is best described as a dilute mixture of chemical compounds (aqueous) or if the waste should be considered organic, containing high levels of organic compounds or a separate nonaqueous organic phase. These two different types of waste matrices influence the degree of partitioning that will occur from the waste to the air. Partitioning describes the affinity that a constituent has for one phase (for example, air) relative to another phase (for example, water) that drives the volatilization of organic chemicals. The choice of waste matrix will significantly affect the rate of emissions from the waste. See Section 2.2 for a more detailed discussion of

Table 2-2. Input Parameters for Landfills

Input Parameter	Units	Default Value	Range ^a	Basis
Unit Design and Operating Parameters				
Biodegradation toggle	none	off		
Operating life of landfill	yr	none	>0	Required input
Total area of landfill - all cells	m ²	none	81–8.09E+6	Required input
Average depth of landfill cell	m	none	>0	Required input
Total number of cells in landfill	unitless	none	≥ 1	Required input
Average annual quantity of waste disposed	Mg/yr	none	>0	Required input
Waste Characterization Information				
Dry bulk density of waste in landfill	g/cm ³	1.2	>0	ERG and Abt (1992)—uses a default of 1.4 g/cm ³ for waste sludge U.S. EPA (1989)—uses sludge density of 1.01 g/cm ³
Average molecular weight of organic-phase waste	g/mol	none	≥ 1	Required input for organic phase wastes
Total porosity of waste	volume fraction	0.50	>0–<1	U.S. EPA (1991)—input used for all active landfills Coburn et al. (1988)—default input for CHEMDAT8 landfill ERG and Abt (1992)—uses default of 0.40 Schroeder et al. (1994)—halogenated aliphatics used 0.46
Air-filled porosity of waste	volume fraction	0.25	>0–total porosity	U.S. EPA (1991)—input used for all active landfills Coburn et al. (1988)—default input for CHEMDAT8 landfill Schroeder et al. (1994)—halogenated aliphatics used range = 0.16 to 0.31

^a Ranges are inclusive, except for parameters with ranges shown as “>0–x”, which must be greater than zero.

Table 2-3. Input Parameters for Land Application Units

Input Parameter	Units	Default Value	Range ^a	Basis
Unit Design and Operating Parameters				
Biodegradation toggle	none	on		
Operating life of land application unit	yr	none	>0	Required input
Tilling depth of land application unit	m	none	>0	Required input
Surface area of land application unit	m ²	none	81–8.09E+6	Required input
Average annual quantity of waste applied	Mg/yr	none	>0	Required input
Number of applications per year	yr ⁻¹	none	≥ 1	Required input
Waste Characterization Information				
Dry bulk density of waste/soil mixture	g/cm ³	1.3	>0	Loehr et al. (1993)—reports density = 1.39 g/cm ³ for surface soil U.S. EPA (1992)—uses a default value of 1.4 g/cm ³ for sewage sludge/soil in land application unit Li and Voudrias (1994)—wet soil column density = 1.03 g/cm ³
Average molecular weight of organic-phase waste	g/mol	none	≥ 1	Required input for organic-phase wastes
Total porosity of waste/soil mixture	volume fraction	0.61	>0–<1	U.S. EPA (1991)—default input used for all model land application units Coburn et al. (1988)—default input for CHEMDAT8 land application units U.S. EPA (1992)—uses default of 0.4 Loehr et al. (1993)—reports porosity = 0.49 for surface soil Li and Voudrias (1994)—wet soil column porosity = 0.558
Air-filled porosity of waste/soil	volume fraction	0.5	>0–total porosity	U.S. EPA (1991)—default input used for all model land application units Coburn et al. (1988)—default input for CHEMDAT8 land application units

^a Ranges are inclusive, except for parameters with ranges shown as “>0–x”, which must be greater than zero.

Table 2-4. Input Parameters for Waste Piles

Input Parameter	Units	Default Value	Range ^a	Basis
Unit Design and Operating Parameters				
Biodegradation toggle	none	off		
Operating life of waste pile	yr	none	>0	
Height of waste pile	m	none	1–10	Required input
Surface area of waste pile	m ²	none	20– 1.3E+6	Required input
Average annual quantity of waste added to waste pile	Mg/yr	none	>0	Required input
Dry bulk density of waste	g/cm ³	1.4	>0	ERG and Abt (1992)—uses default of 1.4 g/cm ³ for waste sludge U.S. EPA (1991)—uses default of 1.8 g/cm ³ for waste pile Coburn et al. (1988)—uses “liquid in fixed waste” density of 1.16 g/cm ³ U.S. EPA (1989)—uses sludge density of 1.01 g/cm ³
Waste Characterization Information				
Average molecular weight of waste	g/mol	none	≥ 1	Required input for organic phase wastes
Total porosity of waste	volume fraction	0.5	>0–<1	U.S. EPA (1991)—input used for all model waste piles Coburn et al. (1988)—default input for CHEMDAT8 waste piles
Air-filled porosity of waste	volume fraction	0.25	>0–total porosity	U.S. EPA (1991)—input used for all model waste piles Coburn et al. (1988)—default input for CHEMDAT8 waste piles

^a Ranges are inclusive, except for parameters with ranges shown as “>0–x”, which must be greater than zero.

waste matrices and partitioning. A general rule of thumb is that wastes that consist of 10 percent or more organics are best modeled as organic phase.

The molecular weight of the organic phase of the waste is a key input for modeling emissions from organic-phase wastes (this is the molecular weight of the bulk liquid, not the individual chemical). Higher waste molecular weights will result in higher emissions estimates. The range of molecular weights for common organic chemicals that might be found in Industrial D wastes spans an order of magnitude, from about 30 g/mol to about 300 g/mol. Therefore, setting this value as accurately as possible will produce the most accurate emissions estimates. In risk mode, no default value is provided; however, Appendix B of the *IWAIR User's Guide* provides an equation for estimating an appropriate molecular weight from the concentrations and molecular weights of the components of the waste. Because these components may include chemicals not being modeled in a particular IWAIR run, IWAIR cannot calculate this directly from user inputs and chemical properties. In allowable concentration mode, the molecular weight of the organic phase is set to the molecular weight of the individual chemical modeled, simulating emissions from pure component.

CHEMDAT8 is fairly sensitive to the total porosity and air porosity values that are used. Total porosity includes air porosity and the space occupied by oil and water within waste or soil. Total porosity is related to bulk density of the waste (which is also an input) as follows:

$$\epsilon_t = 1 - \frac{BD}{\rho_s} \quad (2-12)$$

where

$$\begin{aligned} \epsilon_t &= \text{total porosity (unitless)} \\ BD &= \text{bulk density (g/cm}^3\text{)} \\ \rho_s &= \text{particle density (g/cm}^3\text{)}. \end{aligned}$$

A typical value for ρ_s is 2.65 g/cm³ (Mason and Berry, 1968). Default values are provided for waste bulk density, total porosity, and air-filled porosity, but the user is strongly encouraged to enter site-specific data, if available.

Meteorological Conditions. Two meteorological parameters are used as inputs to CHEMDAT8: annual average wind speed and annual average temperature. By default, IWAIR uses the annual average temperature and wind speed for the meteorological station identified as most representative for the site location. However, the user may override these with site-specific data.

The temperature is used for several calculations to adjust chemical properties that are dependent on temperature. These include the vapor-liquid equilibrium partition coefficient and the gas-phase diffusivity. The temperature correction adjustment for vapor-liquid equilibrium partition coefficient uses the Antoine's coefficients to calculate a ratio of the constituent's vapor pressure at the system temperature to the constituent's vapor pressure at 25°C. This ratio is used

to adjust the vapor-liquid partition coefficient when either Raoult's law or Henry's law is used. The Henry's law coefficient is sometimes estimated by the constituent vapor pressure divided by solubility. Although it is more correct to consider the liquid-phase activity coefficient, it is more difficult to assess a temperature adjustment factor for the liquid-phase activity coefficient (or solubility) than for vapor pressure. In addition, solubility is generally less temperature-dependent than vapor pressure. There has been some progress in developing temperature-dependent correlations for Henry's law coefficients in recent years,³ but these correlations were not readily available at the time of the development of CHEMDAT8, and they are still not currently available for the range of chemicals modeled by IWAIR. Therefore, the best approach for adjusting the Henry's law constants from input values determined at 25°C to the prevailing temperature of the WMU is to use the temperature correction factors developed for vapor pressure, which are based on Antoine's coefficients.

Wind speed is used to select the most appropriate empirical emission correlation equation in CHEMDAT8; there are several of these correlations, and each one applies to a specific range of wind speeds and unit sizes. The CHEMDAT8 model is insensitive to wind speeds for long-term emission estimates from land-based units.

2.3.3 Input Parameters for Surface Impoundments

The input parameters for surface impoundments are presented in Table 2-5.

Unit Design Data. The annual waste quantity (flow rate), the dimensions of the surface impoundment, and whether or not the impoundment is aerated are critical input parameters for impoundments. Because these are so critical and because the values of these parameters for a specific unit to be modeled should be readily available to the user, no default values are provided for these parameters. Operating life is also included here. This value is used to cap the default exposure durations used by IWAIR (30 years for residents and 7.2 years for workers) if the operating life is shorter than the relevant default exposure duration.

Also in this category is the biodegradation toggle. This option, in conjunction with the active biomass input, allows the user to determine what type of biodegradation is modeled. In biologically active surface impoundments, two processes occur: growth of biomass, which provides a growing matrix for chemical adsorption and loss through settling, and direct biodegradation of chemical constituents as the bacteria that form the biomass consume constituent mass. Direct biodegradation cannot occur if there is no active biomass. If an impoundment is biologically active, it may go through a transitional period during which there is active biomass (so adsorption and settling losses occur), but the biomass is not yet adapted to consume the specific chemicals present (so direct biodegradation is not occurring). This transitional period will usually end as the biomass acclimates and adapts to the chemicals present.

By default, biodegradation is set to |ON| for surface impoundments. This toggle controls direct biodegradation. Setting biodegradation to |OFF| turns off direct biodegradation, but does

³ e.g., the compilations of Sanders; see <http://www.mpch-mainz.mpg.de/~sander/res/henry.html>

Table 2-5. Input Parameters for Surface Impoundments

Input Parameter	Units	Default Value	Range ^a	Basis
Unit Design Data				
Biodegradation toggle	none	on		
Operating life	yr	none	>0	Required input
Depth of liquid in surface impoundment	m	none	>0	Required input
Surface area of surface impoundment	m ²	none	81–8.09E+6	Required input
Average annual flow rate	m ³ /yr	none	>0	Required input
Aeration Data				
Fraction of surface area agitated	unitless	none	>0-1	Required input for aerated units
Submerged air flow rate	m ³ /s	none	>0	Required input for diffused air aeration
Mechanical Aeration Information				
Oxygen transfer rate	lb O ₂ /h-hp	3	>0	U.S. EPA (1991)—range = 2.9 to 3.0 lb O ₂ /h-hp
Number of aerators	unitless	none	≥ 1	Required input for mechanically aerated impoundments
Total power input to all aerators	hp	none	>0.25	U.S. EPA (1991)—input for medium-sized, aerated surface impoundments - model units T02I and T02J
Power efficiency of aerators ^b	fraction	0.83	>0-1	U.S. EPA (1991)—range = 0.80 to 0.85
Aerator impeller diameter	cm	61	>0– 100* $\sqrt{\text{WMU area}}$	U.S. EPA (1991)—input used for all model surface impoundments
Aerator impeller rotational speed	rad/s	130	>0	U.S. EPA (1991)—input used for all model surface impoundments
Waste Characteristic Data				
Average molecular weight of waste	g/mol	none	≥ 1	Required input for organic-phase wastes
Density of waste	g/cm ³	none	>0	Required input for organic-phase wastes

(continued)

Table 2-5. (continued)

Input Parameter	Units	Default Value	Range^a	Basis
Active biomass concentration (as mixed-liquor volatile suspended solids (MLVSS)) in the surface impoundment	g/L	0.05	0–1,000	Coburn et al. (1988)—default value used for surface impoundments in developing biodegradation rate constants U.S. EPA (1994a)—recommended default for quiescent surface impoundments; suggests a default for aerated surface impoundments = 0.25 g/L
Total suspended solids (TSS) in surface impoundment influent	g/L	0.2	0–1,000	U.S. EPA (1994a)—range = 0.11–0.40 for surface impoundments designed for biodegradation
Total organics (total organic carbon or chemical oxygen demand) in surface impoundment influent	mg/L	200	0–1,000,000 ^c	
Total biorate	mg/g biomass-h	19	≥0	U.S. EPA (1994a)—default value recommended in CHEMDAT8

^a Ranges are inclusive, except for parameters with ranges shown as “>0–x”, which must be greater than zero.

^b Power efficiency is a misnomer that is carried over from CHEMDAT8. This input is really the oxygen correction factor for the liquid-phase turbulent mass transfer coefficient (see Equation 2-63). The actual power efficiency, used in the equation for gas-phase turbulent mass transfer coefficient (see the equation for power number in the list of parameters for Equation 2-64), is hardwired to a value of 0.85 in CHEMDAT8. In order to maintain consistency with CHEMDAT8, IWAIR also terms this input “power efficiency” but uses it as the oxygen correction factor and hardwires the real power efficiency with a value of 0.85. The default value provided in the IWAIR model and the parameter guidance provided in Appendix B of the *IWAIR User’s Guide* for this input are consistent with its use as the oxygen correction factor.

^b Must be greater than or equal to the sum of the concentrations of all organic chemicals specified as being in the waste by the user in risk calculation mode.

not affect adsorption loss. Setting active biomass to zero turns off biomass growth, so that adsorption losses are limited to adsorption to inlet solids. Setting active biomass to zero also turns off direct biodegradation, as biodegradation cannot occur without active biomass. IWAIR enforces this if the user sets biodegradation to |ON| and then sets active biomass to zero by automatically resetting the biodegradation option to |OFF|.

Aeration. Factors that have an impact on the relative surface area of turbulence and the intensity of that turbulence are important in determining the rate of volatilization of the chemicals in aerated surface impoundments. IWAIR can model two types of aeration, either separately or in combination: mechanical aeration and diffused air aeration.

Mechanical aeration is achieved using impellers rotating in the impoundment and agitating the liquid. Diffused air aeration is achieved through the use of diffusers that force air through the liquid, thus agitating the liquid. The extent and intensity of the turbulence are important factors in estimating emissions from aerated impoundments. For both types of aeration, the fraction of the surface area that is turbulent is an important input and no default is provided.

For mechanical aeration, the model has several input parameters that have an impact on the degree and intensity of the turbulence created by the aeration (or mixing). Total power, power per aerator (number of aerators), and impeller diameter have some impact on the emission results. A default value is provided for impeller diameter; but the user is encouraged to enter a site-specific value, if available. No default is provided for number of aerators or total power. The other parameters, such as impeller speed, power efficiency, and oxygen transfer rate have only a slight impact on the estimated emissions; default values are provided for these inputs, but the user is encouraged to enter site-specific values, if available.

For diffused air aeration, the key input is the submerged air flow. No default is provided for this parameter. The diffused air portion of CHEMDAT8 does not include correlations for calculating a turbulent mass transfer coefficient to account for increased emissions as a result of surface turbulence caused by the air flow through the liquid. However, the equations for turbulent mass transfer coefficient for mechanically aerated systems can be (and are) used to estimate this by entering inputs for a “virtual” aerator. IWAIR uses the default values for impeller diameter, impeller speed, power efficiency, and oxygen transfer rate to create a virtual aerator for diffused air systems. The total power and number of aerators are set based on the size of the unit. This is discussed in more detail in Section 2.4.4.4.

Waste Characterization Inputs. In order to generate an accurate estimate of a constituent’s volatile emissions, a user of IWAIR must define the physical and chemical characteristics of the waste that will be managed in the WMU. In particular, the user must determine if the waste is best described as a dilute mixture of chemical compounds (aqueous) or if it should be considered organic, containing high levels of organic compounds or a separate nonaqueous organic phase. These two different types of waste matrices influence the degree of partitioning that will occur from the waste to the air. Partitioning describes the affinity that a constituent has for one phase (for example, air) relative to another phase (for example, water) that drives the volatilization of organic chemicals. The choice of waste matrix will significantly

affect the rate of emissions from the waste. See Section 2.2 for a more detailed discussion of waste matrices and partitioning. A general rule of thumb is that wastes that consist of 10 percent or more organics are best modeled as organic phase. CHEMDAT8 (and IWAIR) can model both aqueous- and organic-phase wastes for nonaerated (quiescent) surface impoundments, but can model only aqueous-phase wastes for aerated surface impoundments.

CHEMDAT8 includes an input for the fraction of waste that is “oily” (i.e., organic). In IWAIR, if the user models an organic waste, IWAIR assumes that this fraction is 1.

The molecular weight of the organic phase of the waste is a key input for modeling emissions from organic-phase wastes (this is the molecular weight of the bulk liquid, not the individual chemical). Higher waste molecular weights will result in higher emissions estimates. The range of molecular weights for common organic chemicals that might be found in Industrial D wastes spans an order of magnitude, from about 30 g/mol to about 300 g/mol. Therefore, setting this value as accurately as possible will produce the most accurate emissions estimates. In risk mode, no default value is provided; however, Appendix B of the *IWAIR User's Guide* provides an equation for estimating an appropriate molecular weight from the concentrations and molecular weights of the components of the waste. Because these components may include chemicals not being modeled in a particular IWAIR run, IWAIR cannot calculate this directly from user inputs and chemical properties. In allowable concentration mode, the molecular weight of the organic phase is set to the molecular weight of the individual chemical modeled, simulating emissions from pure component.

The density of the waste is also needed for modeling emissions from organic-phase wastes. In risk mode, no default value is provided; however, Appendix B of the *IWAIR User's Guide* provides an equation for estimating an appropriate density from the concentrations and densities of the components of the waste. Because these components may include chemicals not being modeled in a particular IWAIR run, IWAIR cannot calculate this directly from user inputs and chemical properties. In allowable concentration mode, the density of the organic phase is set to 1 g/cm³, consistent with the assumption that 1,000,000 mg/L is pure component.

Factors that influence the rate of biodegradation are important in determining emissions from surface impoundments. Unlike the biodegradation rate model that is used for land application units, landfills, and waste piles, the biodegradation rate model used in CHEMDAT8 for surface impoundments is dependent on the amount of active biomass in the WMU. Therefore, the active biomass concentration is a critical parameter for impoundments (see the discussion above on biodegradation toggle and how it interacts with active biomass). A default value is provided for active biomass if the user chooses to model biodegradation, but the user is encouraged to enter a site-specific value, if available. No default value is provided if the user chooses not to model biodegradation; unless users explicitly want to model the transitional period before the biomass has adapted to the chemicals present, they should set active biomass to zero when the biodegradation toggle is set to |OFF|.

The TSS and total organics in the influent and the total biorate have an impact on the rate of biomass production and subsequently the amount of constituent that is adsorbed onto the solids. These inputs, however, have little or no impact on the estimated emission rates for most

of the constituents included in IWAIR. Default values are provided, but the user is strongly encouraged to enter site-specific values, if available.

Typically, active biomass in the impoundment will be less than TSS in the influent. However, this might not be the case in all situations. The most frequent exception would be in activated sludge units where a portion of the effluent biomass is recovered and recirculated back into the unit. There may also be occasions where the biomass growth rate exceeds the solids settling rate within the unit so that the in-basin active biomass concentration is greater than the influent TSS concentration without a return activated sludge. These conditions are less frequent for surface impoundments than for tanks, which cannot be modeled using IWAIR.

Meteorological Conditions. Two meteorological parameters are used as inputs to CHEMDAT8: annual average wind speed and annual average temperature. By default, IWAIR uses the annual average temperature and wind speed for the meteorological station identified as most representative for the site location. However, the user may override these with site-specific data.

Emissions estimates for nonaerated impoundments are influenced by both temperature and wind speed. Emissions for aerated impoundments are predominantly driven by the turbulent area and associated mass transfer coefficients; therefore, the emissions from aerated impoundments are not strongly affected by the wind speed; they are affected by temperature. Wind speed is used to select the most appropriate correlation equation for calculating the liquid-phase quiescent mass transfer coefficient.

The temperature is used for several calculations to adjust chemical properties that are dependent on temperature. These include the vapor-liquid equilibrium partition coefficient and the gas-phase diffusivity; however, temperature also affects the liquid-phase diffusivity and the liquid-phase turbulent mass transfer coefficient. The temperature correction adjustment for vapor-liquid equilibrium partition coefficient uses the Antoine's coefficients to calculate a ratio of the constituent's vapor pressure at the system temperature to the constituent's vapor pressure at 25°C. This ratio is used to adjust the vapor-liquid partition coefficient when either Raoult's law or Henry's law is used. The Henry's law coefficient is sometimes estimated by the constituent vapor pressure divided by solubility. Although it is more correct to consider the liquid-phase activity coefficient, it is more difficult to assess a temperature adjustment factor for the liquid-phase activity coefficient (or solubility) than for vapor pressure. In addition, solubility is generally less temperature-dependent than vapor pressure. There has been some progress with temperature-dependent correlations for Henry's law coefficients in recent years,⁴ but these were not readily available at the time of the development of CHEMDAT8, and they are still not currently available for the range of chemicals modeled by IWAIR. Therefore, the current temperature correction factor applied to the Henry's law constants based on the temperature dependence of constituent's vapor pressure as estimated using Antoine's equation remains the best approach for adjusting the Henry's law constants (input values determined at 25°C) to the prevailing temperature of the WMU. Depending on the residence time of the waste in the impoundment, the temperature of the waste is not expected to vary significantly with changing

⁴ e.g., the compilations of Sanders; see <http://www.mpch-mainz.mpg.de/~sander/res/henry.html>

atmospheric temperatures. Therefore, annual average temperatures are used to estimate the average waste temperature in the impoundment.

2.4 Mathematical Development of Emissions

This section describes how the inputs described in Section 2.3 are used to calculate the mass emission rate for use in subsequent risk estimates. Most of the mathematical equations used to calculate emissions were taken from the CHEMDAT8 emission model developed by EPA. The documentation of the CHEMDAT8 model can be accessed from EPA's Web site (<http://www.epa.gov/ttn/chief/software.html>, then select "Water8 and Chemdat8"). For convenience, the necessary equations are provided here. For a more detailed discussion or derivation of these equations, the reader is referred to the CHEMDAT8 model documentation (U.S. EPA, 1994a). Some additional equations were needed to convert the CHEMDAT8 fraction emitted to mass emission rates. Through the remainder of this section, the subsection heads indicate whether the equations in that subsection came from CHEMDAT8 or were added by IWAIR.

2.4.1 Landfills

Inputs and assumptions. The basic assumptions used for modeling landfills are as follows:

- The landfill operates for t_{life} years filling N cells of equal size sequentially.
- The active cell is modeled as being instantaneously filled at time $t = 0$, and remains open for t_{life}/N years; this is the time it takes to fill one landfill cell.
- Emissions are only calculated for one cell for t_{life}/N years (it is assumed that the cell is capped after t_{life}/N years and that the emissions from the capped landfill cells are negligible); the time of calculation is calculated as follows:

$$t_{calc} = \frac{t_{life} \times 365.25 \times 24 \times 3,600}{N_{cells}} \quad (2-13)$$

where

t_{calc}	=	time of calculation (s)
t_{life}	=	lifetime of unit (yr)
N_{cells}	=	total number of cells (unitless)
365.25	=	unit conversion (d/yr)
24	=	unit conversion (h/d)
3,600	=	unit conversion (s/h).

- The waste is homogeneous, with an initial concentration of 1 mg/kg for the allowable concentration mode or a user-specified concentration for the risk mode; the landfill may also contain other wastes with different properties.
- Loading is calculated from the annual waste quantity and the size of the landfill, as follows:

$$L = \frac{Q_{\text{annual}} \times t_{\text{life}}}{A_{\text{total}} \times d_{\text{total}}} \quad (2-14)$$

where

$$\begin{aligned} L &= \text{waste loading rate (Mg/m}^3 = \text{g/cm}^3) \\ Q_{\text{annual}} &= \text{annual waste quantity (Mg/yr)} \\ A_{\text{total}} &= \text{total area of unit (m}^2) \\ d_{\text{total}} &= \text{total depth of unit (m).} \end{aligned}$$

Note that if the unit is a monofill receiving only the waste modeled, the loading should equal the bulk density entered by the user. If the unit receives other wastes in addition to the waste modeled, the loading should be less than the bulk density of the waste. The loading cannot exceed the bulk density of the waste; if this condition occurs, the user will get an error message and will be required to change the inputs to eliminate this condition.

- Landfill **cell** areas and depth are used for the model run: $A_{\text{cell}} = A_{\text{total}} / N_{\text{cells}}$; $d_{\text{cell}} = d_{\text{total}}$.
- By default, biodegradation is not modeled for landfills, but the user may choose to turn biodegradation on. If the user chooses to model it, biodegradation is modeled as a first-order process based on soil half-life data.

Calculation of the equilibrium partition coefficient (CHEMDAT8). The emissions from the landfill are based primarily on the vapor-phase concentration of the pore-space gas within the landfill (in equilibrium with the disposed waste) and the diffusion rate of the constituents in this pore-space gas to the soil surface. The vapor-phase concentration is determined by the vapor-liquid equilibrium coefficient (K_{eq}). The calculation of this coefficient is dependent on the type of waste managed.

For organic-waste matrices, the vapor-liquid equilibrium coefficient is based on the constituent's partial vapor pressure (often referred to as Raoult's law), as follows:

$$K_{eq} = \frac{T_{\text{corr}} P_{\text{vap}} MW_{\text{waste}} \epsilon_a}{RTL} \quad (2-15)$$

where

K_{eq}	=	vapor-liquid equilibrium coefficient for constituent (g/cm^3 per g/cm^3)
T_{corr}	=	temperature correction factor for vapor pressure for constituent (unitless)
P_{vap}	=	pure component vapor pressure of constituent at 25°C (atm)
MW_{waste}	=	average molecular weight of the waste (g/mol)
ϵ_a	=	air-filled porosity (cm^3/cm^3)
R	=	universal gas constant = $82.1 \text{ cm}^3\text{-atm}/\text{mol}\text{-}^\circ\text{K}$
T	=	temperature of the system ($^\circ\text{K}$).

The temperature correction factor is based on the ratio of the constituent's vapor pressure, as calculated using Antoine's equation at the system's temperature, and the constituent's vapor pressure at the reference temperature for which the vapor pressure is provided, which is assumed to be 25°C in IWAIR (that is, all chemical properties in the IWAIR database correspond to the property value at 25°C). The temperature correction factor is calculated as follows:

$$T_{corr} = 10^{\left(VP_b \left(\frac{-1}{VP_c + T - 273.15} + \frac{1}{VP_c + 25} \right) \right)} \quad (2-16)$$

where

VP_b	=	Antoine's vapor pressure constant B for constituent
VP_c	=	Antoine's vapor pressure constant C for constituent.

The Antoine's constants used in IWAIR assume the Antoine's equation (which is $\log P_{vap} = A - B/(C + T)$) and are developed for calculating the vapor pressure, P_{vap} , in mmHg given the temperature, T , in °C.

For aqueous matrices, the vapor-liquid equilibrium coefficient is based on the constituent's Henry's law constant, as follows:

$$K_{eq} = \frac{T_{corr} MW_{waste} \epsilon_a}{RTL} \left(\frac{10^6}{18} \right) \quad (2-17)$$

where

H	=	Henry's law constant at 25°C ($\text{atm}\text{-m}^3/\text{mol}$)
MW_{waste}	=	average molecular weight of the waste = 18 g/mol = molecular weight of water
18	=	unit conversion factor for aqueous waste ($\text{cm}^3/\text{mol} = 18 \text{ g/mol} \times 1 \text{ cm}^3/\text{g}$)
10^6	=	unit conversion factor (cm^3/m^3).

Calculation of the effective diffusivity (CHEMDAT8). The effective diffusivity of constituent in a porous medium is calculated as follows:

$$D_{\text{eff}} = D_a \frac{\epsilon_a^{3.33} T_{C,\text{gas}}}{\epsilon_t^2} \quad (2-18)$$

where

$$\begin{aligned} D_{\text{eff}} &= \text{effective diffusivity of constituent in the system (cm}^2\text{/s)} \\ D_a &= \text{diffusivity of constituent in air at 25}^\circ\text{C (cm}^2\text{/s)} \\ T_{C,\text{gas}} &= \text{temperature correction factor for gas diffusivity (unitless)} \\ &= (T / 298.15)^{1.75} \\ \epsilon_t &= \text{total porosity (cm}^3\text{/cm}^3\text{).} \end{aligned}$$

Calculation of the fraction emitted (CHEMDAT8). The equation used to calculate the fraction emitted is dependent on the volatilization rate constant, the biodegradation rate constant, and the time period for the calculation. The volatilization rate constant is calculated as follows:

$$K_v = \frac{K_{\text{eq}} D_{\text{eff}}}{d_{\text{wmu}}^2} \quad (2-19)$$

where

$$\begin{aligned} K_v &= \text{volatilization rate constant for constituent (1/s)} \\ d_{\text{wmu}} &= \text{characteristic depth of the WMU (cm) = } d_{\text{total}} / 100 \text{ for a landfill.} \end{aligned}$$

The fraction emitted is calculated using one of the following three solution algorithms, depending on the biodegradation (b_{soil}) and volatilization rate (K_v) constants.

If $K_v / b_{\text{soil}} < 0.1089$,

$$f_{\text{emitted}} = \left(\frac{K_v}{b_{\text{soil}}} \right)^{0.5} \left[1 - e^{-t_{\text{calc}} \left(\frac{\pi^2}{4} K_v + b_{\text{soil}} \right)} \right] \quad (2-20)$$

If $K_v / b_{\text{soil}} \geq 0.1089$ and $K_v t_{\text{calc}} < 0.22$ (short-term solution),

$$f_{\text{emitted}} = 2 \left(\frac{K_v t_{\text{calc}}}{\pi} \right)^{0.5} \left[1 - \frac{t_{\text{calc}} b_{\text{soil}}}{3} \right] \quad (2-21)$$

If $K_v / b_{soil} \geq 0.1089$ and $K_v t_{calc} \geq 0.22$ (first term of the Taylor series expansion solution),

$$f_{emitted} = \frac{8}{\pi^2} \left(\frac{1 - e^{-t_{calc} \left(\frac{\pi^2}{4} K_v + b_{soil} \right)}}{1 + \frac{4}{\pi^2} \left(\frac{b_{soil}}{K_v} \right)} \right) + 0.1878 \quad (2-22)$$

where

$$\begin{aligned} f_{emitted} &= \text{fraction of constituent emitted to the atmosphere (unitless)} \\ b_{soil} &= \text{soil biodegradation rate constant for constituent (1/s).} \end{aligned}$$

Calculation of the fraction biodegraded (CHEMDAT8). The fraction biodegraded and the fraction emitted are both dependent on the volatilization and biodegradation rate constants, and their values are not independent of each other. The fraction biodegraded is calculated using one of the following two equations depending on the biodegradation and volatilization rate constants, as follows:

If $K_v t_{calc} < 0.22$ (short-term solution),

$$f_{bio} = 1 - \left(1 - 2 \left(\frac{K_v t_{calc}}{\pi} \right)^{0.5} \left[e^{-t_{calc} b_{soil}} \right] \right) - f_{emitted} \quad (2-23)$$

If $K_v t_{calc} \geq 0.22$ (first term of the Taylor series expansion solution),

$$f_{bio} = 1 - \left(1 - \left[\frac{8}{\pi^2} \left(1 - e^{-t_{calc} \left(\frac{\pi^2}{4} K_v \right)} \right) + 0.1878 \right] \left[e^{-t_{calc} b_{soil}} \right] \right) - f_{emitted} \quad (2-24)$$

where

$$f_{bio} = \text{fraction of constituent biodegraded in the WMU (unitless).}$$

Calculation of the emission flux rate (IWAIR). The average emission flux rate for the landfill can be calculated as follows:

$$E = \frac{Q_{annual} \times C_{waste} \times L \times f_{emitted}}{A_{cell} \times \rho_b \times 365.25 \times 24 \times 3,600} \quad (2-25)$$

where

E	=	emission flux rate of constituent ($\text{g}/\text{m}^2\text{-s}$)
C_{waste}	=	concentration of constituent in waste ($\text{mg}/\text{kg} = \text{g}/\text{Mg}$)
A_{cell}	=	area of cell (m^2)
ρ_b	=	bulk density of waste in landfill (g/cm^3)
365.25	=	unit conversion (d/yr)
24	=	unit conversion (h/d)
3,600	=	unit conversion (s/h).

2.4.2 Land Application Units

Inputs and assumptions. The assumptions used for modeling land application units are as follows:

- Waste application occurs N_{appl} times per year. The land application unit is modeled using time steps equal to the time between applications, as follows:

$$t_{\text{calc}} = \frac{365.25 \times 24 \times 3,600}{N_{\text{appl}}} \quad (2-26)$$

where

N_{appl}	=	number of applications per year (yr^{-1})
365.25	=	unit conversion (d/yr)
24	=	unit conversion (h/d)
3,600	=	unit conversion (s/h).

- The land application unit operates for t_{life} years and is modeled for t_{life} plus 30 years, in order to account for up to 30 years of postclosure exposure. The total number of time steps modeled is thus

$$N_{\text{steps}} = (t_{\text{life}} + 30) \times N_{\text{appl}} \quad (2-27)$$

where

N_{steps}	=	total number of time steps modeled (unitless)
t_{life}	=	operating life of unit (yr).

This total number of time steps, N_{steps} , cannot exceed 32,766 because of code limitations for integer variables. This is unlikely to result in practical limitations, unless the operating life is very long and the number of applications per year very

high. For example, daily applications (365 applications/year) for 59 years would still be within this limitation.

- The waste is homogeneous, with an initial concentration of 1 mg/kg for the allowable concentration mode or a user-specified concentration for the risk mode.
- Loading is calculated from the annual waste quantity and the size of the land application unit as follows:

$$L = \frac{Q_{\text{annual}} \times 100}{N_{\text{appl}} \times A \times d_{\text{till}}} \quad (2-28)$$

where

L	=	loading rate (Mg/m ³ = g/cm ³)
Q _{annual}	=	annual quantity of waste (Mg/yr)
A	=	area of unit (m ²)
d _{till}	=	tilling depth (cm)
100	=	unit conversion (cm/m).

- By default, biodegradation is modeled as a first-order process based on soil half-life data. The user may choose to turn biodegradation off.
- The characteristic depth of a land application unit used in Equation 2-19 (calculation of K_v) is the tilling depth ($d_{\text{wmu}} = d_{\text{till}}$).
- The volume of the land application unit remains constant. To maintain this assumption, it is assumed that as more waste is applied, an equal volume of waste/soil mixture is buried or otherwise removed from the active tilling depth.

The equipment used to incorporate and mix the waste with the soil in a land application unit typically does so at a fixed depth; therefore, the depth of waste incorporation is fixed. If the depth of waste added to the unit over the active life of the land application unit is significant relative to the tilling depth, subsequent applications of waste will leave the bottom-most layer of contaminated soil untilled (i.e., buried). If subsequent waste applications were added to the same fixed mass of soil, the model as constructed would perceive this as adding a fixed quantity of pure constituent to the fixed soil mass during each waste application. As such, the land application unit could eventually have higher constituent concentrations than the applied waste (for compounds that persist in the environment). Therefore, the burial loss term is needed for an accurate estimate of the maximum steady-state soil concentration (and emissions rate) according to mass balance principles.

IWAIR further assumes that this buried waste layer does not have any significant impact on the emission estimates. There are several reasons why the buried waste is not expected to contribute significantly to the emissions. At the time of burial, the buried waste constituent concentration is less than (or at most equal to) the constituent concentration in the tilled layer of the land application unit. Secondly, experience with emission estimates of buried waste using model equations developed by Jury et al. (1990) shows that the buried waste layer contributions to emissions are typically 1 to 2 orders of magnitude less than the emissions from the surface layer (depending on the relative depths of each layer) when the initial concentrations are homogeneous (a requirement for the Jury model solution). Constituent burial tends to be a significant constituent removal mechanism only when other constituent removal mechanisms are essentially zero (i.e., chemicals that do not degrade or volatilize). Constituent loss in buried waste is a simplifying assumption with respect to volatilization, but this assumption provides a much better simulation of the land application unit constituent exposure scenarios than when waste burial is not included. Without “burial” losses, land application unit soil concentrations can exceed those in the original waste material. These “unlikely” high soil concentrations provide greater errors in the estimated long-term volatilization rates than are projected by the land application unit model with constituent burial losses.

Calculation of fraction emitted and fraction biodegraded (CHEMDAT8). The IWAIR model calculates the fraction emitted and the fraction biodegraded for each chemical in the land application unit using the CHEMDAT8 equations shown in Equations 2-15 through 2-24, as applicable, for the time interval between applications (i.e., the time of the calculation, t_{calc} , from Equation 2-26). The calculation is made for the first application given the inputs and assumptions outlined above. As the model is linear (first-order) with respect to constituent concentration, the fraction emitted and the fraction biodegraded are independent of the starting concentration. Consequently, these calculated fractions can be applied to successive waste applications assuming that the volume of the land treatment unit remains constant; this assumption is also documented above. The IWAIR model takes the fraction emitted and fraction biodegraded and calculates the long-term emissions that occur from successive use. This is an enhancement made in IWAIR and is documented in the following subsections.

Calculation of the emission rate (IWAIR). The emission rate for a land application unit is dependent on the starting concentration or mass of constituent within the land application unit for a given application. For the first application, the mass of constituent in the land application unit just after the first application is

$$M_{start,1} = M_{appl} = \frac{Q_{annual} \times C_{waste}}{N_{appl}} \quad (2-29)$$

where

$$M_{start,1} = \text{mass of chemical in unit at start of time step 1 (g)}$$

$$\begin{aligned} M_{\text{appl}} &= \text{mass of chemical added during one application (g)} \\ C_{\text{waste}} &= \text{concentration of chemical in waste (mg/kg = g/Mg)}. \end{aligned}$$

The mass of constituent in the land application unit at the end of the first time of calculation (just prior to more waste being added) is

$$M_{\text{end},1} = M_{\text{appl}} \times (1 - f_{\text{emitted}} - f_{\text{bio}}) \quad (2-30)$$

where

$$\begin{aligned} M_{\text{end},1} &= \text{mass of chemical in unit at end of time step 1 (g)} \\ f_{\text{emitted}} &= \text{fraction emitted (unitless).} \\ f_{\text{bio}} &= \text{fraction biodegraded (unitless).} \end{aligned}$$

Note that fraction emitted and fraction biodegraded, which are calculated according to Equations 2-20 through 2-24, are not independent of each other despite their appearance as separate terms in the above equation. Fraction emitted depends on biodegradation rate and other variables, and fraction biodegraded depends on biodegradation rate and fraction emitted, among other variables.

The generalized equation for the starting mass of constituent (just after any waste application number, n , and taking into account the “burial” loss needed to maintain a constant land application unit volume) is

$$M_{\text{start},n} = M_{\text{appl}} + M_{\text{end},n-1} \times \left(1 - \frac{d_{\text{appl}}}{d_{\text{till}}} \right) \quad (2-31)$$

where

$$\begin{aligned} M_{\text{start},n} &= \text{mass of chemical in unit at start of time step } n \text{ (g)} \\ M_{\text{end},n-1} &= \text{mass of chemical in unit at end of time step } n-1 \text{ (g)} \\ d_{\text{appl}} &= \text{depth of waste applied (cm), see Equation 2-32.} \end{aligned}$$

Depth of waste applied is calculated as

$$d_{\text{appl}} = \frac{Q_{\text{annual}} \times 100}{N_{\text{appl}} \times \rho_b \times A} \quad (2-32)$$

where

$$\rho_b = \text{bulk density of waste (g/cm}^3 = \text{Mg/m}^3\text{)}.$$

Note that d_{till} must exceed d_{appl} and should probably be at least three to four times d_{appl} . The user will be warned if d_{till} does not exceed d_{appl} .

The generalized equation for the ending mass of constituent in the land application unit for any waste application number, n , (just prior to the $n+1$ waste application) is

$$M_{end,n} = M_{start,n} \times (1 - f_{emitted} - f_{bio}) \quad (2-33)$$

where

$M_{end,n}$ = mass of chemical in unit at end of time step n (g).

The generalized equation for the mass of constituent emitted during any application period (time of calculation) is

$$M_{emitted,n} = M_{start,n} \times f_{emitted} \quad (2-34)$$

where

$M_{emitted,n}$ = mass of chemical emitted in time step n (g).

For each time period, the emission flux rate is calculated as follows:

$$E_n = \frac{M_{emitted,n}}{t_{calc} \times A} \quad (2-35)$$

where

E_n = emission flux rate in time step n (g/m²-s).

The starting mass, ending mass, and emitted mass of constituent are calculated for each time step for a period equal to the life of the unit plus 30 years. This time series of emission rates for each time step must then be converted to a time-averaged emission rate for a time period corresponding to exposure assumptions. Three exposure scenarios are possible: for carcinogenic risk, IWAIR uses an average for a time period that corresponds to the exposure duration: 30 years for a resident or 7 years for a worker. For noncarcinogens, IWAIR uses a 1-year average as an indicator of the highest exposure experienced over a chronic duration.

The additional 30 years postclosure are modeled to ensure that the period of maximum emissions is captured. For chemicals that tend to volatilize quickly, this is likely to occur during operation of the unit, as new waste additions continue to be made. For chemicals that do not tend to volatilize quickly, but build up in the unit, this is likely to occur postclosure (when waste

additions stop and the maximum concentration is achieved in the unit). To capture the maximum period, IWAIR calculates all possible 30-year and 7-year averages over the life of the unit plus 30 years and chooses the maximum of these. For example, for a unit with an operating life of 10 years, eleven 30-year averages are possible, the first starting in year 1 of operation and running through 10 years of operation and 20 years postclosure, and the last starting in the first year postclosure (i.e., year 11) and running for 30 years.

The emission rate displayed on the emission screen in IWAIR and in the printed reports for all chemicals modeled is the maximum 1-year average used for noncarcinogens. However, the air concentration displayed on the RESULTS screen and in the printed reports is based on the appropriate average emission rate for the chemical and receptor. If a chemical has both a carcinogenic and a noncarcinogenic health benchmark (so that both risk and HQ are calculated), the air concentration displayed on the RESULTS screen corresponds to the carcinogenic risk calculation, not the noncarcinogenic HQ calculation. The interested user can use Equation 6-1 to convert displayed 1-year emission rates to the corresponding 1-year air concentration for such chemicals. Similarly, Equation 6-1 can be used to convert the 30- or 7-year air concentration to the corresponding emission rate (which is not displayed).

2.4.3 Waste Piles

Inputs and assumptions. The modeling assumptions used for modeling waste piles are as follows:

- The waste pile is modeled as a batch process with the waste remaining in the waste pile for one average residence time (see time of calculation equation provided in Equation 2-36). The model solution is appropriate for either of the following two scenarios:
 1. The waste pile is instantaneously filled at time $t = 0$ and remains dormant (no other waste added) for one average residence time, at which time the entire waste pile is emptied and completely filled with fresh waste.
 2. An annual quantity of waste is added to the waste pile consistently (in small quantities) throughout the year, and a corresponding quantity of the oldest waste within the waste pile is removed from the waste pile (so that the waste pile is essentially a plug-flow system).
- The waste is homogeneous, with an initial concentration of 1 mg/kg for the allowable concentration mode or a user-specified concentration for the risk mode.
- By default, biodegradation is not modeled for waste piles. Waste piles are not generally designed for biodegradation; however, if residence times of waste in the waste pile are on the order of months or years, naturally occurring microorganisms could potentially acclimate and degrade constituents within the waste pile. The wastes for which IWAIR was designed are industrial wastes, not hazardous wastes (and so presumably are not toxic enough to fail the Toxicity Characteristics

Leaching Procedure, because that would make them hazardous). Therefore, while a specific waste might not be very conducive to biomass growth, it cannot be widely assumed that the wastes for which this model was designed would be toxic to any potential biomass. Therefore, the user has the option of turning biodegradation on if site-specific conditions suggest that biodegradation is occurring. If the user chooses to model it, biodegradation is modeled as a first-order process based on soil half-life data.

- Loading is the bulk density of the waste material ($L = \rho_b$).
- The time of calculation is equal to one average residence time of waste in the waste pile. The time of calculation (or residence time) is calculated as follows:

$$t_{\text{calc}} = \frac{A \times h \times \rho_b \times 365.25 \times 24 \times 3,600}{Q_{\text{annual}}} \quad (2-36)$$

where

t_{calc}	=	time of calculation (s)
A	=	area of unit (m^2)
h	=	height of waste pile (m)
ρ_b	=	bulk density of waste ($\text{g}/\text{cm}^3 = \text{Mg}/\text{m}^3$)
Q_{annual}	=	annual waste quantity (Mg/yr)
365.25	=	units conversion (d/yr)
24	=	units conversion (h/d)
3,600	=	units conversion (s/h).

- The waste pile geometry is modeled as a square box. The sides are assumed to be essentially vertical and are assumed to be negligible in the overall surface area of the waste. The shape of the upper surface is assumed to be square. The area and height of this box are both user inputs and are used by the emissions component.

Calculation of fraction emitted and fraction biodegraded (CHEMDAT8). The IWAIR model calculates the fraction emitted and the fraction biodegraded for each chemical in the waste pile using Equations 2-15 through 2-24, as applicable, for one residence time (i.e., the time of the calculation, t_{calc} , from Equation 2-36).

Calculation of the emission flux rate (IWAIR). The average emission flux rate for the waste pile can be calculated as follows:

$$E = \frac{Q_{\text{annual}} \times C_{\text{waste}} \times f_{\text{emitted}}}{A \times 365.25 \times 24 \times 3,600} \quad (2-37)$$

where

E	=	emission flux rate of constituent ($\text{g/m}^2 \cdot \text{s}$)
C_{waste}	=	concentration of constituent i in waste ($\text{mg/kg} = \text{g/Mg}$)
f_{emitted}	=	fraction of constituent i emitted to the atmosphere (unitless)
365.25	=	units conversion (d/yr)
24	=	units conversion (h/d)
3,600	=	units conversion (s/h).

2.4.4 Surface Impoundments

Inputs and Assumptions. The basic modeling assumptions used for modeling surface impoundments are somewhat different for aqueous- and organic-phase wastes. For aqueous-phase wastes, assumptions include

- The impoundment operates under steady-state, well-mixed conditions (continuously stirred tank reactor (CSTR)). In a CSTR, the unit is assumed to be perfectly (or completely) mixed so that the concentration within the unit is at all times homogeneous and equal to the effluent concentration. Constituent in the influent waste stream is assumed to be instantaneously and evenly distributed within the unit. This modeling assumption is generally appropriate when aeration or mechanical mixing is present. It may also be generally applicable for certain nonaerated units whose general dimensions and orientation to prevailing winds afford significant mixing from eddy currents. An alternate model construct is the plug-flow model, which is roughly equivalent to a batch reactor. In a plug-flow system, essentially no mixing is assumed. This scenario is most appropriate for units that are quiescent and whose dimensions and orientation to prevailing winds limit wind-caused mixing (e.g., a very narrow, long, slow-moving stream). In reality, both model constructs are imperfect. Complete mixing or absolutely no mixing is never achieved. For IWAIR, it was determined that the complete mixing model construct was generally the most applicable; it was therefore used for IWAIR. Consequently, the predicted emissions for aqueous-phase wastes are most accurate for well-mixed units and are less accurate when little or no mixing (i.e., plug-flow) is present.
- Hydrolysis rate is first order with respect to constituent concentrations.
- By default, aqueous waste constituent biodegradation is modeled as first order with respect to biomass concentrations and follows Monod kinetics with respect to constituent concentrations (see discussion of the biodegradation rate constants K_I and K_{max} in Section 2.3.1). Because the Monod kinetic model is nonlinear with respect to the constituent concentration, waste influent concentration is calculated using an iterative approach (using a Newton-Raphson routine) for the concentration calculation mode or is user-specified for the risk calculation mode. The surface area, depth, flow rate, and aeration parameters (if applicable) are all

directly specified for the model unit. See Section 6.2.2 for further discussion of the Newton-Raphson method.

In addition to constituent biodegradation, growth of biomass occurs in biologically active surface impoundments, which provides a growing matrix for chemical adsorption and loss through settling. Adsorption and settling losses also occur in the absence of active biomass and biodegradation, but are limited to occurring on inlet solids. Biodegradation cannot occur if there is no active biomass. If an impoundment is biologically active, it may go through a transitional period during which there is active biomass (so biomass growth occurs, facilitating adsorption and settling losses) but the biomass is not yet adapted to consume the specific chemicals present (so biodegradation does not occur). This transitional period will usually end as the biomass acclimates and adapts to the chemicals present.

The user can control these two processes (biodegradation and adsorption losses) separately. Setting biodegradation to |OFF| turns off biodegradation, but does not affect adsorption loss. Setting active biomass to zero turns off biomass growth, so that adsorption losses are limited to adsorption to inlet solids. Because biodegradation cannot occur in the absence of active biomass, setting active biomass to zero also effectively turns off biodegradation.

For organic-phase wastes (which can be modeled only for nonaerated impoundments), assumptions include

- The impoundment is assumed to operate under steady-state, plug-flow (no mixing) conditions.
- There is no biodegradation or hydrolysis for organic-phase wastes.
- There is no adsorption modeled for organic-phase wastes.

The equations for surface impoundments are presented in the following five sections: Section 2.4.4.1, Quiescent Surface Impoundments for Aqueous-Phase Wastes; Section 2.4.4.2, Quiescent Surface Impoundments for Organic-Phase Wastes; Section 2.4.4.3, Mechanically Aerated Surface Impoundments (Aqueous-Phase Wastes Only); Section 2.4.4.4, Diffused Air Aerated Surface Impoundments (Aqueous-Phase Wastes Only); and Section 2.4.4.5, Both Mechanically and Diffused Air Aerated Surface Impoundments (Aqueous-Phase Wastes Only).

2.4.4.1 Quiescent Surface Impoundments for Aqueous-Phase Wastes

Calculation of the liquid-phase mass transfer coefficient for quiescent surface impoundments (CHEMDAT8). The appropriate correlation to use to estimate the liquid-phase mass transfer coefficient for quiescent surface impoundments is dependent on the wind speed and the fetch-to-depth ratio of the impoundment. The fetch is the linear distance across the WMU, and it is calculated from the WMU's surface area assuming a circular shape for the WMU. That is,

$$F = \left(\frac{4 A}{\pi} \right)^{0.5} \quad (2-38)$$

where

F = fetch of the unit (m)
A = surface area of the unit (m²).

For wind speeds less than 3.25 m/s, the following correlation is used to calculate the liquid-phase mass transfer coefficient for quiescent surface impoundments regardless of the fetch-to-depth ratio:

$$k_{l,q} = 2.78 \times 10^{-6} T_{c,liq} \left(\frac{D_w}{D_{ether}} \right)^{\frac{2}{3}} \quad (2-39)$$

where

$k_{l,q}$ = liquid-phase mass transfer coefficient for quiescent surface impoundments (m/s)
 $T_{c,liq}$ = temperature correction factor for liquid-phase mass transfer coefficients (unitless) = (T / 298.15)
T = temperature of system (°K)
 D_w = diffusivity of constituent in water (cm²/s)
 D_{ether} = diffusivity of ether in water (8.5E-6 cm²/s).

For wind speeds greater than or equal to 3.25 m/s, the appropriate correlation for the liquid-phase mass transfer coefficient for quiescent surface impoundments is dependent on the fetch-to-depth ratio (F/d_{liq}) as follows:

$$\text{For } \frac{F}{d_{liq}} < 14,$$

$$k_{l,q} = T_{c,liq} (1.0 \times 10^{-6} + (a \times 10^{-4}) (U^*)^b Sc_{liq}^{-0.5}) \quad (2-40)$$

$$\text{For } 14 \leq \frac{F}{d_{liq}} \leq 51.2,$$

$$k_{l,q} = T_{c,liq} \left[2.605 \times 10^{-9} \left(\frac{F}{d_{liq}} \right) + 1.277 \times 10^{-7} \right] U_{10}^2 \left(\frac{D_w}{D_{ether}} \right)^{\frac{2}{3}} \quad (2-41)$$

For $\frac{F}{d_{liq}} > 51.2,$

$$k_{l,q} = 2.611 \times 10^{-7} T_{c,liq} U_{10}^2 \left(\frac{D_w}{D_{ether}} \right)^{\frac{2}{3}} \quad (2-42)$$

where

- d_{liq} = depth of liquid in the surface impoundments (m)
- a = equation constant, $a = 34.1$ for $U^* > 0.3$ m/s; $a = 144$ for $U^* < 0.3$ m/s
- U^* = friction velocity (m/s) $= 0.01U (6.1 + 0.63U)^{0.5}$
- U_{10} = wind speed 10 m above surface (m/s)
- b = equation constant, $b = 1$ for $U^* > 0.3$ m/s; $b = 2.2$ for $U^* < 0.3$ m/s
- Sc_{liq} = liquid-phase Schmidt number $= \mu_w / (\rho_w D_w)$
- μ_w = viscosity of water (g/cm-s) $= 9.37E-3$ g/cm-s
- ρ_w = density of water (g/cm³) $= 1$ g/cm³.

Calculation of gas-phase mass transfer coefficient for quiescent surface impoundments (CHEMDAT8). The gas-phase mass transfer coefficient for quiescent surface impoundments is estimated as follows:

$$k_{g,q} = (4.82 \times 10^{-3}) T_{c,gas} U^{0.78} Sc_g^{-0.67} F^{-0.11} \quad (2-43)$$

where

- $k_{g,q}$ = gas-phase mass transfer coefficient for quiescent surface impoundments (m/s)
- $T_{c,gas}$ = temperature correction factor for gas diffusivity or gas mass transfer coefficient (unitless) $= (T / 298.15)^{1.75}$
- T = temperature of system (°K)
- Sc_g = gas-phase Schmidt number $= \mu_a / (\rho_a D_a)$
- ρ_a = density of air (g/cm³) $= 1.2E-3$ g/cm³
- μ_a = viscosity of gas (air) (g/cm-s) $= 1.81E-4$ g/cm-s
- D_a = diffusivity of constituent in air (cm²/s).

Calculation of overall mass transfer coefficient for quiescent surface impoundments for (CHEMDAT8). For aqueous wastes, the overall mass transfer coefficient that determines the rate of volatilization is determined based on a two-resistance model: a liquid-phase mass transfer resistance and a gas-phase mass transfer resistance. The overall volatilization mass transfer coefficient for quiescent surface impoundments is calculated as follows:

$$K_{OL} = K_{OL,q} = \left(\frac{1}{k_{l,q}} + \frac{1}{K_{eq} k_{g,q}} \right)^{-1} \quad (2-44)$$

where

- K_{OL} = overall volatilization mass transfer coefficient (m/s)
 $K_{OL,q}$ = overall mass transfer coefficient for quiescent surface impoundments (m/s)
 K_{eq} = vapor-liquid equilibrium coefficient for constituent (g/cm³ per g/cm³).

Generally, Henry's law is used to estimate the vapor-liquid equilibrium coefficient for aqueous systems. The only exception to this is when the constituent is present within the surface impoundments at concentrations above the aqueous solubility. As the aqueous solubility is determined for binary systems (i.e., the constituent in pure water), a chemical's solubility in the waste matrix within the surface impoundments may be quite different than its solubility in pure water. However, Henry's law applies to dilute solutions. The aqueous solubility is used as an indication of whether or not the solution is "dilute" for a given chemical. As the steady-state concentration within the impoundment has not been calculated and cannot be calculated without first estimating the overall mass transfer coefficient, the vapor-liquid equilibrium coefficient is calculated based on Henry's law as follows:

$$K_{eq} = \frac{T_{corr} H}{RT} \quad (2-45)$$

where

- T_{corr} = temperature correction factor for vapor pressure for constituent (unitless) (see Equation 2-16)
 H = Henry's law constant at 25°C (atm-m³/mol)
 R = universal gas constant = 8.21E-5 m³-atm/mol-°K
 T = temperature of the system (°K).

If the concentration within the impoundment exceeds the aqueous solubility for a given constituent based on the initial Henry's law assumption, then the vapor-liquid equilibrium partition coefficient for that chemical is recalculated using Raoult's law as follows:

$$K_{eq} = \frac{T_{corr} P_{vap}}{RT} \left(\frac{18}{10^6} \right) \quad (2-46)$$

where

- P_{vap} = vapor pressure of constituent at 25°C (atm)
 T = temperature of the system (°K)
 18 = unit conversion factor for aqueous waste (cm³/mol = 18 g/mol × 1 cm³/g)
 10^6 = unit conversion factor (cm³/m³).

Calculation of adsorption rate constant (CHEMDAT8). Sorption onto solids within the surface impoundment is a competing removal mechanism to the volatilization loss. The sorption removal rate depends on the rate at which solids enter and/or are produced within the surface impoundment and the solids-liquid partition coefficient. Solids production within the

surface impoundment is dependent on either the available degradable organic matter entering the surface impoundments or the maximum overall biodegradation rate of this organic matter. The solids “wasting” rate (r_{TSS}) is the total rate at which solids enter the surface impoundment plus the rate of solids production within the surface impoundment, and it is calculated as follows:

$$r_{TSS} = 1000TSS_{in} Q + 0.5 \times \min \left(\frac{r_{b,tot}}{3600} 1.046^{2 \times (T-298)} d_{liq} A X; C_{TOC} Q \right) \quad (2-47)$$

where

r_{TSS}	=	total solids wasting rate (g solids/s)
1000	=	unit conversion factor (L/m ³)
TSS_{in}	=	total suspended solids in influent (g/L)
Q	=	influent flow rate (m ³ /s)
0.5	=	assumed biomass yield coefficient (g solids/g organic consumed)
min()	=	function that returns the minimum value of a series of numbers separated by semicolons
$r_{b,tot}$	=	biodegradation rate for total organics (mg/g-hr)
3600	=	unit conversion (s/hr)
0.001	=	unit conversion (g/mg)
T	=	temperature (°K)
X	=	active biomass concentration in the surface impoundment (g/L)
C_{TOC}	=	concentration of total organics in the surface impoundment influent (mg/L) = g/m ³ .

It is assumed that the sludge is 99 percent water by weight and 1 percent solids by weight and that the sludge has a density essentially that of water (i.e., 1 g/cm³). The sludge-liquid partition coefficient, therefore, adjusts the solid-liquid partition coefficient as follows:

$$K_s = 0.99 + 0.01K_d \quad (2-48)$$

where

K_s	=	sludge-liquid partition coefficient (g/cm ³ sludge per g/cm ³ waste)
K_d	=	solid-liquid partition coefficient (cm ³ /g solids).

For organic compounds, the following correlation is used to estimate the solid-liquid partition coefficient using the constituent's octanol-water partition coefficient as follows:

$$K_d = 10^{0.67 \log(K_{ow})} + 0.39 \quad (2-49)$$

where

K_{ow}	=	octanol-water partition coefficient (unitless).
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For mercury, the solid-liquid partition coefficient (K_d) is directly input in place of the octanol-water partition coefficient, and Equation 2-48 is used directly using this input value for K_d .

The adsorption rate constant is then calculated as

$$K_{ads} = \frac{100K_s r_{TSS}}{10^6 d_{liq} A} \quad (2-50)$$

where

K_{ads} = adsorption rate constant (1/s)
 100 = sludge solids correction factor, (100 g sludge/g solids) \times (1 cm³/g sludge)
 10⁶ = units correction factor (cm³/m³).

Calculation of effluent concentration (CHEMDAT8). All aqueous surface impoundments are modeled as well-mixed systems so that the concentration within the surface impoundment is assumed to be the same as the effluent concentration. Because of the nonlinear biodegradation rate model used for aqueous surface impoundments, the steady-state solution for the effluent concentration (and concentration within the surface impoundment) requires the solution of a quadratic equation, as follows:

$$C_{liq} = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad (2-51)$$

where

C_{liq} = constituent concentration in the surface impoundment and in the effluent (mg/L = g/m³)
 a,b,c = quadratic equation terms, which are defined in the following equations:

Quadratic term a:

$$a = \frac{1}{t_{res}} + \frac{K_{OL}}{d_{liq}} + K_{hyd} + K_{ads} \quad (2-52)$$

where

t_{res} = hydraulic residence time (s) = $d_{liq} \times A/Q$
 K_{hyd} = hydrolysis rate constant (1/s).

Quadratic term b:

$$b = a \left(\frac{K_{max}}{K_1} \right) + 1.046^{(T-298)} \left(\frac{K_{max} X}{3600} \right) - \frac{C_{in}}{t_{res}} \quad (2-53)$$

where

K_{\max}	=	maximum biodegradation rate constant (mg/g-hr)
K_1	=	first-order biodegradation rate constant (g/L-hr)
T	=	temperature ($^{\circ}\text{K}$)
3600	=	units conversion factor (s/hr)
C_{in}	=	constituent concentration in surface impoundment influent (mg/L = g/m ³)

Quadratic term c:

$$c = -\left(\frac{K_{\max}}{K_1}\right)\left(\frac{C_{\text{in}}}{t_{\text{res}}}\right) \quad (2-54)$$

Calculation of fraction emitted (CHEMDAT8). The fraction emitted is the mass of constituent volatilized per mass of constituent influent to the surface impoundment:

$$f_{\text{emitted}} = \frac{AK_{\text{OL}}C_{\text{liq}}}{QC_{\text{in}}} \quad (2-55)$$

where

f_{emitted} = fraction of constituent emitted to the atmosphere (unitless).

Calculation of fraction adsorbed (CHEMDAT8). The fraction adsorbed is the mass of constituent adsorbed per mass of constituent influent to the surface impoundment:

$$f_{\text{adsorbed}} = \frac{A d_{\text{liq}} K_{\text{ads}} C_{\text{liq}}}{Q C_{\text{in}}} \quad (2-56)$$

where

f_{adsorbed} = fraction of constituent adsorbed (unitless).

Calculation of emission flux rate (IWAIR). The emission flux rate is calculated as follows:

$$E = \frac{f_{\text{emitted}} QC_{\text{in}}}{A} = K_{\text{OL}} C_{\text{liq}} \quad (2-57)$$

where

E = emission flux rate of constituent (g/m²-s).

2.4.4.2 Quiescent Surface Impoundments for Organic-Phase Wastes.

Biodegradation, hydrolysis, and adsorption are not modeled for organic-phase wastes.

Calculation of gas-phase mass transfer coefficient for quiescent surface impoundments (CHEMDAT8). The gas-phase mass transfer coefficient for quiescent surface impoundments is estimated as follows:

$$k_{g,q} = (4.82 \times 10^{-3}) T_{c,gas}^{0.67} U^{0.78} Sc_g^{-0.67} F^{-0.11} \quad (2-58)$$

where

T = temperature of system ($^{\circ}K$).

Calculation of overall mass transfer coefficient for organic systems (CHEMDAT8).

For organic wastes, the liquid-phase mass transfer coefficient is assumed to be noncontrolling. The liquid-phase mass transfer correlations presented previously for aqueous surface impoundments assume the liquid is water, and these are not applicable to an impoundment containing organic (i.e., nonaqueous) wastes. Consequently, the overall mass transfer coefficient for organic systems is calculated based on the gas-phase mass transfer coefficient and the equilibrium partition coefficient as follows:

$$K_{OL,org} = K_{eq} k_{g,q} \quad (2-59)$$

where

$K_{OL,org}$ = overall mass transfer coefficient for organic waste (m/s).

The vapor-liquid equilibrium coefficient is calculated using Raoult's law similarly to the vapor-liquid equilibrium coefficient for aqueous systems when Raoult's law is used (Equation 2-46), except the unit conversion factor for aqueous waste is now calculated based on the organic waste properties as follows:

$$K_{eq} = \frac{T_{corr} P_{vap}}{RT} \left(\frac{MW}{\rho_{liq} 10^6} \right) \quad (2-60)$$

where

T = temperature of the system ($^{\circ}K$)
 MW = molecular weight of the organic waste (g/mol)
 ρ_{liq} = density of organic waste (g/cm³)
 10^6 = unit conversion factor (cm³/m³).

Calculation of fraction emitted (CHEMDAT8). There are no other loss mechanisms for organic systems besides volatilization and the surface impoundment effluent. The fraction emitted is calculated based on a plug-flow model solution as follows:

$$f_{\text{emitted}} = 1 - e^{\left(\frac{-AK_{\text{OL,org}}}{Q}\right)} \quad (2-61)$$

Calculation of emission flux rate (IWAIR). The emission flux rate is calculated as follows:

$$E = \frac{f_{\text{emitted}} QC_{\text{in}}}{A} = K_{\text{OL}} C_{\text{liq}} \quad (2-62)$$

2.4.4.3 Mechanically Aerated Surface Impoundments (Aqueous-Phase Wastes Only). Mechanical aeration is effected by impellers or mixers that agitate the surface of impoundment. Correlations are available to estimate the turbulent mass transfer coefficients for these agitated surfaces based on the power input to the aerators, the impeller size, the rotation speed, and so forth. These correlations are presented below. Although the agitated surface area may extend well beyond the diameter of the aerator impeller, there is usually some portion of the surface impoundment surface area that is not affected by the aerators and that remains quiescent. The overall quiescent mass transfer coefficient for these areas is calculated exactly as it is for quiescent impoundments (Equation 2-38 through Equation 2-46).

Note that organic-phase wastes cannot be modeled for aerated impoundments; the CHEMDAT8 oily film model used to model organic-phase wastes in nonaerated surface impoundments is not applicable to aerated impoundments, as the aeration breaks up the organic film modeled.

Calculation of the liquid-phase mass transfer coefficient for turbulent surface impoundments (CHEMDAT8). The liquid-phase mass transfer coefficient for turbulent surface impoundments is calculated as

$$k_{l,t} = T_{c,liq} \left(\frac{8.22 \times 10^{-3} \text{ J } P_{\text{tot}} 1.024^{(T-20)} O_{cf} \text{ MW}_w}{10.76 A_t \rho_l} \right) \left(\frac{D_w}{D_{O_2,w}} \right)^{0.5} \quad (2-63)$$

where

- $k_{l,t}$ = liquid-phase mass transfer coefficient for turbulent surface impoundments (m/s)
- J = oxygen transfer rate (lb O₂/h-hp)
- P_{tot} = total power to the impellers (hp)
- T = liquid temperature in WMU (°C)

- O_{cf} = oxygen correction factor⁵ (unitless)
 MW_w = molecular weight of water (g/mol) = 18 g/mol
 A_t = surface area for affected by the aeration (i.e., turbulent) (m²) = $A \times f_{aer}$
 A = surface area of surface impoundment (m²)
 f_{aer} = fraction of total surface impoundment surface area affected by aeration (unitless)
 $D_{O_2,w}$ = diffusivity of oxygen in water (cm²/s) = 2.4E-5 cm²/s.

Calculation of the gas-phase mass transfer coefficient for turbulent surface impoundments (CHEMDAT8). The gas-phase mass transfer coefficient for turbulent surface impoundments is calculated as

$$k_{g,t} = 1.35 \times 10^{-7} T_{c,gas} Re_g^{1.42} p^{0.4} Sc_g^{0.5} Fr^{-0.21} D_a MW_a d_{imp}^{-1} \quad (2-64)$$

where

- $k_{g,t}$ = gas-phase mass transfer coefficient for turbulent surface areas (m/s)
 Re_g = gas-phase Reynolds number = $(d_{imp}^2 w \rho_a) / \mu_g$
 p = power number = $0.85 (550 P_{tot} / N_{aer}) g_c / [(62.428 \rho_w) w^3 (d_{imp} / 30.48)^5]$
 g_c = gravitational constant = 32.17 lb_m-ft/s²-lb_f
 N_{aer} = number of aerators
 w = rotational speed (rad/s)
 Fr = Froude number = $[w^2 (d_{imp} / 30.48)] / g_c$
 MW_a = molecular weight of air (g/mol) = 29 g/mol
 d_{imp} = impeller diameter (cm).

Calculation of the overall turbulent surface mass transfer coefficient (CHEMDAT8). The overall turbulent surface mass transfer coefficient is calculated based on the two-resistance module as follows:

$$K_{OL,t} = \left(\frac{1}{k_{l,t}} + \frac{1}{K_{eq} k_{g,t}} \right)^{-1} \quad (2-65)$$

where

- $K_{OL,t}$ = overall turbulent surface mass transfer coefficient (m/s).

⁵ CHEMDAT8 misnames this input power efficiency. The actual power efficiency, used in the equation for gas-phase turbulent mass transfer coefficient, is hardwired to a value of 0.85 in CHEMDAT8 (see the equation for power number in the list of parameters for Equation 2-64). In order to maintain consistency with CHEMDAT8, IWAIR also terms this input power efficiency and hardwires the real “power efficiency” with a value of 0.85. The default value provided in the IWAIR model and the parameter guidance provided in Appendix B of the *IWAIR User's Guide* for this input are consistent with its use as the oxygen correction factor.

The vapor-liquid partition coefficient is calculated using Equation 2-45 (based on Henry's law) for the initial calculation of the constituent concentration within the surface impoundment. If the constituent concentration within the surface impoundment exceeds the aqueous solubility limit, then the overall mass transfer coefficients are re-calculated using Equation 2-46 for the vapor-liquid partition coefficient (based on Raoult's law).

Calculation of the overall volatilization mass transfer coefficient (CHEMDAT8). The overall volatilization mass transfer coefficient is calculated based on an area-weighted average as follows:

$$K_{OL} = \frac{K_{OL,t} A_t + K_{OL,q} A_q}{A} \quad (2-66)$$

where

$$\begin{aligned} K_{OL,q} &= \text{overall mass transfer coefficient for quiescent surface areas (m/s)} \\ A_q &= \text{quiescent surface area} = (1 - f_{aer}) A \text{ (m}^2\text{)} \text{ (Note: } A_t + A_q \text{ must equal } A\text{).} \end{aligned}$$

Calculation of emission flux rates (IWAIR). Once the overall mass transfer coefficient is calculated, the calculations of the adsorption rate coefficient, effluent constituent concentration, fraction emitted, fraction adsorbed, and emission flux rates follow the equations presented for quiescent, aqueous surface impoundments (Equations 2-47 through Equation 2-57).

2.4.4.4 Diffused Air Aerated Surface Impoundments (Aqueous-Phase Wastes Only).

Diffused air aeration is effected by blowing air through diffusers or spargers located below the liquid surface (typically near the bottom of the impoundment) and allowing the air bubbles to rise through the liquid to the liquid surface. The rising air bubbles are assumed to come into equilibrium with the liquid so that the diffused air acts to "strip" volatiles from the impoundment. Additionally, the rising bubbles tend to agitate and mix the air-liquid interface, increasing the mass transfer (or creating turbulence) between the air and liquid. No correlations have been developed to estimate the "turbulent" mass transfer coefficients when the turbulence is caused by diffused air aeration; therefore, IWAIR assigns "virtual mechanical aerators" to use as inputs for calculating the overall mass transfer coefficient for the turbulent surfaces following the procedures described for mechanically aerated surface impoundments. Again, there is usually some portion of the surface impoundment surface area that is not affected by the aeration and that remains quiescent. The overall quiescent mass transfer coefficient for these areas is calculated exactly as it is for quiescent, aqueous impoundments (Equation 2-38 through Equation 2-46).

Organic-phase wastes cannot be modeled for aerated impoundments; the CHEMDAT8 oily film model used to model organic-phase wastes in nonaerated surface impoundments is not applicable to aerated impoundments, as the aeration breaks up the organic film modeled.

Calculation of emission rate constant for diffused air (CHEMDAT8). The emission rate caused by the "stripping" action of the bubbles rising through the wastewater is calculated assuming that all of the diffused air comes into equilibrium with the wastewater. An effective first-order emission rate constant is calculated for the diffused air constituent loss as

$$K_{\text{diff}} = \frac{K_{\text{eq}} Q_{\text{air}}}{d_{\text{liq}} A} \quad (2-67)$$

where

$$\begin{aligned} K_{\text{diff}} &= \text{emission rate constant for diffused air (1/s)} \\ Q_{\text{air}} &= \text{diffused air flow rate (m}^3\text{/s).} \end{aligned}$$

Again, the vapor-liquid equilibrium partition coefficient is calculated using Equation 2-45 (based on Henry's law) for the initial calculation of the constituent concentration within the surface impoundment. If the constituent concentration within the surface impoundment exceeds the aqueous solubility limit, then the overall mass transfer coefficients are re-calculated using Equation 2-46 for the vapor-liquid partition coefficient (based on Raoult's law).

Calculation of “virtual mechanical aerator” parameters (IWAIR). Diffused air agitates the liquid surface, causing an increased emission rate. This effect is modeled by selecting “virtual mechanical aerator” parameter inputs to be used in calculating the overall turbulent surface area mass transfer coefficient. The algorithms used to calculate the “virtual mechanical aerator” parameters for the diffused-air-only surface impoundments are designed to model a “low” degree of surface turbulence caused by the diffused aeration. If the diffused air system creates a high degree of surface turbulence, the user could develop alternative mechanical aerator inputs and model the unit using the BOTH (DIFFUSED AIR & MECHANICAL) option.

The factor that controls the parameters selected for the virtual mechanical aerator is the turbulent surface area (total surface impoundment area \times fraction agitated). Thus, the fraction-agitated parameter for diffused-air-only surface impoundments has a direct impact on the fraction of the surface area to which the overall turbulent mass transfer coefficient is applied, and to a lesser degree, the actual value of the turbulent mass transfer coefficient.

It is assumed that 10 m² of surface turbulence is generated per horsepower of a typical aerator. The Treatment Storage and Disposal Facility (TSDF) survey (U.S. EPA, 1991) provides data on several model units with mechanical aerators, including total aerator power and turbulent surface area. The values for turbulent surface area per hp for these model units ranges from 3 to 8.4 m²/hp. These units reflect real mechanical aerators; diffused air aerators would typically produce less turbulence over a greater area, so a greater turbulent area per hp is desired for the virtual aerators. Thibodeux (1976) provides a range of 0.11 to 20.1 m²/hp that is typical for mechanically aerated systems. Therefore, a value of 10 m²/hp was selected as greater than the TSDF reported values and roughly the midpoint of the Thibodeux range. The total power input for the virtual mechanical aerator is then calculated as

$$P_{\text{tot}} = \frac{A f_{\text{aer}}}{10} \quad (2-68)$$

where

P_{tot} = total power to the impellers (hp)
 10 = assumed area of agitation per horsepower applied to aerator (m^2/hp).

It is also assumed that the horsepower of a single aerator is not to exceed 15 hp, and the number of aerators should be a whole number. Consequently, the number of aerators is calculated as follows:

$$N_{\text{aer}} = \text{round}\left(\frac{P_{\text{tot}}}{15} + 0.5\right) \quad (2-69)$$

where

$\text{round}()$ = function that rounds the value to the nearest integer
 15 = assumed maximum horsepower of an aerator (hp/aerator)
 0.5 = value used to make the $\text{round}()$ function round up to the next highest integer.

All other aerator parameters (impeller diameter, impeller speed, oxygen transfer rate, and power efficiency) are selected based on the IWAIR default values for these parameters.

Calculation of the overall volatilization mass transfer coefficient (CHEMDAT8). The overall volatilization mass transfer coefficient is calculated as an area-weighted average of the overall quiescent surface area and turbulent surface area mass transfer coefficients (Equation 2-66). These quiescent surface and turbulent surface mass transfer coefficients are calculated as described in Sections 2.4.4.1 and 2.4.4.3, respectively.

Calculation of effluent concentration (CHEMDAT8). The effluent concentration (and the concentration within the surface impoundment) is calculated using Equation 2-51, but the quadratic term a includes the emission rate constant for diffused air as follows:

Quadratic term a for systems with diffused air:

$$a = \frac{1}{t_{\text{res}}} + \frac{K_{\text{OL}}}{d_{\text{liq}}} + K_{\text{hyd}} + K_{\text{ads}} + K_{\text{diff}} \quad (2-70)$$

The equation for the quadratic term b remains unchanged, but it includes the quadratic term a within its equation, so that the value of the quadratic term b term is dependent on the diffused air rate constant (K_{diff}).

Calculation of emission flux rates (IWAIR). The remainder of the calculations (fraction emitted, fraction adsorbed, and emission flux rates) follow the equations presented for quiescent, aqueous surface impoundments (Equations 2-55 through Equation 2-57).

2.4.4.5 Both Mechanically and Diffused Air Aerated Surface Impoundments (Aqueous-Phase Wastes Only). Some surface impoundments operate both mechanical aerators and diffused air aeration. These aerators may be used in separate areas of the surface impoundment, or the mechanical aerators may operate above the diffused air aeration (i.e., mechanically agitating the area where the diffused air bubbles are reaching the liquid surface). This system is modeled exactly like the diffused aeration system, except that the mechanical aerator inputs provided by the user are used rather than the values imputed for the “virtual mechanical aerator.” As such, the IWAIR solution is most applicable for surface impoundments with mechanical aerators placed above the diffused air aeration or for surface impoundments where the degree of turbulence and or the area affected by the diffused air aeration is small in comparison to the mechanically agitated surface. In these cases, the area affected by the mechanical aeration can be used directly to estimate the fraction agitated input parameter (f_{aer}).

The equations used to calculate the emissions from the both mechanical and diffused air aerated surface impoundments follow the method used for diffused-air-only surface impoundments presented in Section 2.4.4.4 (without the need to calculate “virtual mechanical aerator” parameters).

Note that organic-phase wastes cannot be modeled for aerated impoundments; the CHEMDAT8 oily film model used to model organic-phase wastes in nonaerated surface impoundments is not applicable to aerated impoundments, as the aeration breaks up the organic film modeled.